

EXPLORING THE POSSIBLE APPLICATION OF TWO-LEVEL FRACTIONAL FACTORIAL DESIGN IN SANITARY ENGINEERING

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In Partial Fulfilment of the Requirements
for the Degree of
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to the

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DECEMBER, 1973**

C E R T I F I C A T E

This is to certify that this work on
"Exploring the Possible Application of Two-Level
Fractional Factorial Design in Sanitary Engineering"
has been carried out under my supervision and this
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ABSTRACT

To obtain the maximum quantitative knowledge about the influence of various parameters on a process a number of Statistical Experiment Design techniques have been proposed during recent years. The present study was carried out to explore the possible application of one such Experiment-Design Technique to Sanitary Engineering.

Two-Level Quarter Factorial (with Mirror) Design was chosen for this investigation, particularly because of its easy usage and analysis.

The destabilization of suspended particles by coagulation has long been the most significant contributor to the removal of colloidal turbidity of water and hence a process extensively studied experimentally. Hence evaluation of the influence of various coagulation parameters on the efficiency of this process was chosen for this investigation:

The percent turbidity removal was observed against two-level variations of a number of parameters, including initial turbidity, alum dosage, total alkalinity, flocculation time and speed of paddles.

The experimental data obtained by the Two-Level Quarter Factorial design was very well interpreted with respect to existing classical theory for coagulation and flocculation mechanisms.

The levels of significance of influential variables were determined successfully, which are in close conformity with the present day knowledge.

The multiple linear regression analysis of the data enabled to correlate the response to various control parameters. The relationship is of nature similar to hypotheses earlier proposed from time to time by research workers.

NOMENCLATURE

<u>Symbol</u>	<u>Quantity</u>	<u>Units</u>	<u>Dimensions</u>
A	Coagulant Dose	mg/l or moles/l	ML^{-2}
A	Cross-sectional area of the paddles in a plane perpendicular to its direction of motion	M^2	L^2
a	Radius of the particle	micron or mm	L
Cd	Drag Coefficient		Dimensionless
D	Diffusion Coefficient	cm^2/sec	L^2T^{-1}
D	An experimentally determined rate variable which is a function of the particle size distribution in the system ²⁷		Dimensionless
D_o	Diameter of the particle at time $t = c$	micron	L
D	Dielectric constant of the Medium	-	Dimensionless
d	Thickness of double layer or thickness of the zone of influence of the particle charge	\AA^o	L
F_D	Drag force	Kg	MLT^{-2}
$f(a/d)$	Henry's function		Dimensionless
G	Mean Velocity Gradient	sec^{-1}	T^{-1}
J_{PK}	Rate of change in total concentration of particles due to peri-kinetic coagulation	particles/ml/sec	$L^{-3}T^{-1}$

J_{OK}	Rate of change in total concentration of particles due to Ortho-kinetic flocculation	particles/ ml/sec	$L^{-3}T^{-1}$
K	Boltzmann's Constant		ML^2T^{-2}
M	Electrophoretic mobility or velocity per unit potential gradient	microns/sec/ volt/cm	$MT^{-1}V^{-1}L$
N^o	Total concentration of particles in suspension at time 't'	particles/ml	L^{-3}
N^o_0	Initial particle concentration	"	"
η	Collision efficiency factor (fraction of the total number of collisions which are successful in producing aggregates)		Dimensionless
P	Power input to the reactor	foot-lbs/sec	ML^2T^{-3}
Q	Net charge on the colloidal particle or The charge difference between the particle and body of the solution	e.s.u.	Q
T	Absolute Temperature, Flocculation Time	oK , Min	Temp, T
V	Volume of the flocculator	M^3	L^3
V_r	Relative velocity of the particle with respect to the fluid	cm/sec	LT^{-1}
du/dz	Velocity gradient	sec^{-1}	T^{-1}

X

ZP	Zeta Potential	MilliVolts	Volt
μ	Fluid viscosity	lb-sec/ft ²	ML ⁻¹ T ⁻¹
	Volume fraction of colloids (Volume of colloidal particles per unit volume of suspension)		Dimensionless
ϕ	Sticking Ratio ²⁷		Dimensionless
a	Ratio ²⁷ of the collision radius of a particle to its actual radius		"
ψ (psi)	Nerst Potential	MilliVolts	Volts

CHAPTER I

INTRODUCTION

1.0 INTRODUCTION:

The practice of Sanitary Engineering has evolved from empirical field experience. Even the few laboratory studies undertaken largely proceed on empirical lines for development of a quantitative picture of any process. Several methods have been evolved during recent years in other areas of science and technology, to improve the consistency and reliability of conventional field tests, however Sanitary Engineering has still been generally labouring under severe handicap of having nothing like an adequate experimental plan based on rational mathematical approach. Normally designs are based on criteria, developed by field experience or experimental work, which tend to be subjective and empirical. Very often the designer does not have an adequate basis of underlying theory describing the process in terms of the decisions he has to make.

Needless to say that such design practices should have a definite co-relation with theory for better understanding of the process and further improvement in design.

1.1 FRACTIONAL FACTORIAL DESIGN:

One of the methods that has gained wide popularity, in identification and modification of possible inadequacies of commonly used experimental strategies is - Statistical Experimental Design. Research efficiency, that is the amount of meaningful information obtained per unit cost, can be increased significantly by using such experiment design techniques, in particular "Fractional Factorial Design" technique. With the recent staggering challenges in the field of water and wastewater treatment processes, such approaches have become utmost necessary.

Proper design procedure for laboratory experiments should furnish a systematic and controlled means for developing rational experimental plans to determine precise parameter estimates and their interaction with each other at the minimum experimental cost and effort. Precision of the experimental results is a strong function of the design used.

1.2 SELECTION OF THE PROCESS:

There is probably no other phase of water treatment programme that is subject to so many variations in the design, as pre-conditioning of turbid waters, by coagulation and flocculation, prior to filtration. Flocculation has been, and probably will continue to be, the most important tool used by sanitary engineers for removal of coagulant impurities.

Colloidal systems have been the subject of rather intensive investigations and it has been endeavour through the years to make the problem of turbidity removal amenable to a rational mathematical analysis by finding a definite relationship among influent turbidities coagulant dosages, mixing velocities, flocculation periods, settling times, etc. which will provide the most economical solution. In absence of comprehensive qualitative theory, forming a sound foundation for quantitative determination, applicable to complex colloidal systems, proper dosage of the coagulant has often to be established by empirical methods like Jar Test. Current practice of carrying out these Jar tests is tedious, time consuming and involves collection of unnecessarily large number of data. Moreover these tests lead to poor estimation and virtually no understanding of the various parameters and their interaction.

Considering importance of this process, Coagulation-Flocculation was chosen to investigate the applicability of some modern experimental design techniques, specifically "Fractional Factorial Design" technique in Sanitary Engineering investigations.

1.3 COAGULATION & FLOCCULATION:

As there are numerous variables that affect coagulation, a theoretical analysis of a given set of conditions and a prognosis of coagulation resulting therefrom is practically impossible. The discovery of any systematic relationships

among the measurable variables that affect coagulation, therefore must ultimately result in better understanding of the coagulation mechanisms and also in an increased ability to predict the effect of a given set of conditions.

Every experiment has to be conducted against a background environment of prior knowledge. Research into coagulation and flocculation phenomena by Chemists/Sanitary Engineers has well established the validity of certain important parameters through empirical relationships. Considering various limitations, effects of certain important variables like initial turbidity, coagulant dosage, flocculation time, speed of paddles, Flocculation Time on turbidity removal was studied over a limited experimental region.

1.4 OBJECTIVES OF THE STUDY:

The purpose of this study thus essentially was, to describe a statistical experimental design based on 2-level fractional factorial design procedure for planning and analysis of Jar tests. The techniques presented can, of course, be readily extended to more complicated problems.

The first phase of the investigation was to identify the key parameters of significance in turbidity removal by coagulation and flocculation. The second phase of investigation was to study, in more detail, how these variables are inter-related, and to express their inter-relationships in the form of equations.

CHAPTER II

2.1 WATER TREATMENT

2.01 INTRODUCTION:

Next to air, the other essential requirement for human life to exist is water. Raw water available in different sources contains various kinds of impurities in varying amounts. Natural surface waters, polluted either by man or nature, are likely to contain dissolved inorganic and organic substances, biological forms, such as bacteria, other microorganisms, planktons, and suspended inorganic materials⁴¹. These impurities tend to render the water unfit for domestic, municipal or industrial uses (as steam generation, brewing, dyeing, etc.)³⁰.

2.02 OBJECTIVES:

The primary objective⁵⁰ of water treatment is to eliminate impurities to such an extent that the water becomes suitable for the use to which it is to be put up. The character and degree of treatment processes¹⁶ used in any specific instance depend upon the initial quality and nature of the raw water, and the standards of quality to be attained after treatment. The need for such treatments is ever increasing because of the additional pollution contributed by expanding industrial complexes and an ever demanding human population.

Raw water may require treatment for removing the pathogenic organisms, unpleasant tastes and odors, hardness, iron and manganese, corrosive substances, color, turbidity, etc.

2.03 TREATMENT PROCESSES:

Treatment involves physical, chemical and biological changes that transform raw waters into potable waters. The most widely used unit treatment processes³³ for removal of different impurities include plain sedimentation, coagulation generally followed by filtration, and chemical precipitation, used generally to remove dissolved minerals like hardness components and iron and manganese. Other processes³⁰ such as adsorption, aeration, ion exchange, oxidation, and distillation are also important for the removal of dissolved substances. Above mentioned unit treatment processes are usually followed in the same sequence, thus each one of them prepares water for next one which results in improving the efficiencies of each of them and hence overall efficiency of the plant also.

2.04 COAGULATION & FLOCCULATION:

Destabilization of suspended particles by coagulation and flocculation,³⁷ generally followed by sedimentation and filtration, is by far the most widely used combination to remove - (1) the substances producing turbidity (inorganic and organic) in water; (2) color, true and apparent, (3) harmful bacteria and other pathogens, (4) algal and other plankton

organisms, and (5) taste- and odor-producing substances.

2.05 CHEMICAL TREATMENT OF SEWAGE AND INDUSTRIAL WASTES:

Chemical coagulation is also used to some extent in sewage and industrial waste treatments. A few typical examples serve to illustrate the extent to which effective coagulation is necessary for efficient water and wastewater treatment.

2.05.1 Suspended solids in sewage^{38,5} - Analyses of domestic sewage (Hunter and Henkelekina, 1965) shows that about 80% of chemical oxygen demand in raw domestic sewage is attributable to material which is colloidal or larger in size. Certain types of industrial wastewaters³⁵ may also contain even greater fractions of particulate matter. Chemical treatment for the removal of phosphorus, frequently results in the formation of colloidal precipitates; which require aggregation. The effectiveness of oxidation ponds²⁶ for the removal of soluble nutrients requires that algae be removed from the pond effluents. Effective disposal of waste sludges³⁵ is often accomplished by coagulation followed by cake filtration or centrifugation.

2.05.2 Colored wastes³² - Wastewaters from textile dyeing and finishing are ideal examples of wastes containing high concentration of color. Chemical coagulation is the most widely used method for treating such wastes and in certain situations affected upto 99% color removal.

2.05.3 Oil-bearing wastes³² - These wastes are also being treated by chemical coagulation.

2.06 MERITS & DEMERITS OF COAGULATION:

The principal assets¹³ of coagulation are ease of starting and stopping, easy regulation of degree of treatment, and invulnerability to toxic materials. In addition to above coagulation can remove certain materials such as phosphates, which are passed by biological treatment processes.

The principal limitations associated with chemical coagulation are relatively high cost of chemicals, need for complete operation, and limited effectiveness for separation of soluble organic matter.

Chemical coagulation is particularly useful in situations where industrial wastes toxic to bacteria are present in sewage.

2.07 CHARACTERISTICS OF TURBIDITY IN NATURAL WATERS

Turbidity may be caused by a wide variety of inorganic and organic materials, algal or bacterial growth. The suspended materials²⁴ vary in size from colloidal to coarse dispersions, depending upon degree of turbulence. Water existing under relatively quiescent conditions, most of the turbidity will be due to colloidal and extremely fine dispersions. Under flood conditions, most of the turbidity will be due to relatively coarse dispersions. Coarser components, such as sand and silt, have smaller detention times ranging from 0.3 secs. (Gravel

ϕ 10 mm) to 33 min (Silt $\phi = 0.01$ mm), hence can be removed from water by simple sedimentation. The hydraulic settling values of smaller size impurities are very small and they require a long detention time to settle down in plain sedimentation tanks. Thus for descending down through a height of 10 ft. or 3M (the common depth of settling tank), a particle of fine silt (Sp. Gr. 2.65) of size 0.06 mm may take about 1/3 hrs., with a settling velocity of 3.8 mm/sec., while a particle of clay ($\gamma = 2.65$) size 0.002 mm, with a settling velocity of 0.0062 mm/sec. may require about 5.8 days. Colloidal impurities finer than clay particles, e.g. $\angle 0.0001$ mm, are in continuous motion so that they never settle down (or may take infinite time viz. 63 yrs./ft. of settlement) by gravity in medium (water), through which they are dispersed. The long-term stability to remain suspended in water is basically a function of both size and specific gravity. Hence when turbidity in water is due to fine size and colloidal particles (approximately 0.001 to 1 micron), which are too small for gravitational settling alone to be an effective removal process, flocculation, which shall produce large, more readily settleable aggregates, is essential for successful separation by sedimentation. The settling time²³ for suspended matter is summarized in Table 2.07.1.

TABLE 2.07.1: SETTLING CHARACTERISTICS OF SUSPENDED MATTER

	Size mm	Settling velocity mm/sec.	Time required to settle/ft.
Silt	0.01	0.154	33 mts.
Bacteria	0.001	0.00154	55 hrs.
Fine clay particle	0.0001	0.0000154	230 days
Colloidal particle	0.00001	0.000000154	63 yrs.

Turbidity removal is an important consideration in public water supplies for three major reasons⁴¹: Aesthetic, Filtrability, and Disinfection efficiency.

a. Aesthetic - Consumers demand turbid free, sparklingly clear water, because turbid drinking water gives rise to speculation of possible pollution and health hazards.

b. Filtrability - Satisfactory operation of Rapid Sand Filters depend upon effective turbidity removal before filtration. When turbidity of water increases, filtration of water is rendered more costly due to short filter-runs, frequent back-wash because of filter clogging.

c. Disinfection - For effective disinfection, there must be contact between the agent and organisms. In turbid waters, most of the harmful organisms are exposed to the action of the disinfectant. However in cases where turbidity is caused by sewage solids, many of the pathogenic organisms may be encased in the particles and protected from disinfectant.

Thus turbidity removal produces a water that is aesthetically acceptable, more amenable to filtration thru sand filters, and that can be disinfected properly.

Laboratory studies of chemical coagulation are often required to determine the best chemical or combination of chemicals and amounts needed to accomplish a desired objective in water, sewage and industrial waste treatment practices. The results obtained serve as basis for design and of operation of treatment facilities¹⁴.

Coagulation and flocculation being old and well established processes, adequate theoretical knowledge is available to make rational decisions about various design parameters for an effective and efficient plant. Some of these are given in the following sections.

2.2 NATURE OF SUSPENDED MATTER IN WATER:

2.2.1 CLASSIFICATIONS OF TURBIDITY:

Impurities in water vary in size by about six orders of magnitude, from a few Angstroms for soluble substances to a few hundred microns for suspended materials¹⁴. According to Nordell³⁰, any finely divided insoluble impurities, whatever their nature, that may be suspended in and mar the clarity of a water are known collectively as turbidity, and material that is so coarse that it rapidly drops out of suspension, when water loses velocity is termed as "sediment". Suspended matter in water may be classified according to its origin, as inorganic mineral matter or organic carbonaceous material. Substances producing turbidity are often inorganic, while those causing taste, odor, and color are generally organic compounds. Organic materials reaching rivers, serve as food for bacteria and the resulting bacterial growth and other micro organisms that feed upon bacteria~~1~~ produce additional turbidity.

The particles producing turbidity may be further classified according to their size, which may range from molecular dimensions to 50 millimicron or larger. The smaller particles, classified as colloidal, normally range in size from about 1 to 100 millimicron^{38,23}.

The fraction greater than 1 micron in diameter is generally referred to as silt and will settle out rapidly on standing. The colloidal particles will remain suspended for very long times. Smaller the size, higher is the time required for settling²⁴.

For a large particle the ratio of the surface area to mass is low, hence mass effects such as sedimentation under gravity predominate. For colloidal material, where the ratio is very high, surface properties of the particles, such as electric charges, inorganic groups and affinity to adsorb water become more important. The large ratio obtained in colloidal state accounts for increased energy and activity¹².

Colloids have been further classified as lyophobic (hydrophobic) and lyophilic (hydrophilic). In hydrophilic systems (such as starch, gums and proteins), the particles chemically react with water in which they are dispersed and with metal coagulants. Purely hydrophobic systems (hypothetical case) do not react with the water phase, and coagulation is achieved by reactions that are largely physical rather than chemical. Finely divided particles of clay minerals and metal oxides exhibit colloidal characteristics and are largely hydrophobic in nature⁴⁹.

2.3 THE STABILITY OF COLLOIDS.

Stability refers to the inherent property of the colloidal particles to remain dispersed despite long passage

of time. Thermodynamically stable colloidal systems have been termed reversible; thermodynamically unstable colloids are then termed irreversible. Thus a stable colloid is an irreversible (thermodynamically unstable) colloid which aggregates at a very slow rate⁵¹.

It has long been observed that solid colloidal particles in an aqueous dispersion move in an electric field, indicating that these carry an electric charge. The charged colloidal particles in water are subjected to two opposing forces; one producing destabilization or flocculation; the other stabilization or dispersion. The factors producing stabilization (keeping particles apart to form a stable colloidal suspension) are hydration or solvation (results in a shell of water molecules), and electrostatic repulsion. For hydrophilic (water-liking) systems, stability is maintained by the phenomenon of hydration, in which water molecules are attracted and chemically adsorbed on the surface of the particles. Such colloid-water interactions act as a barrier and retard the aggregation of the colloids^{36,51}.

Irreversible colloids (hydrophobic) owe their apparent stability to charge and solvation effects. But it is now generally agreed among colloid scientists that stability of hydrophobic particles is due largely to the phenomenon of electrical double layer²⁸. Charge effects are probably more important and certainly better understood.

An excellent theoretical treatment is given in the treatise by Verwey and Overbeek⁵¹ (1948). These models for the apparent stability of lyophobic colloids are based on charge effects alone and, to the extent that solvation effects are important in natural systems, are unable to characterize such systems. The Verwey-Overbeek model has been summarized, extended, and applied to clays by Van Olphen (1963). Stumm and Morgan (1970) have summarized conceptual models for these charge effects and applied these models to several important phenomena in natural systems and also in treatment processes⁵¹.

Several theories have been advanced to quantitatively describe the concept of the electrical double layer consisting of the charged particle surface and a surrounding sheath of ions of charge opposite to that of the particle surface. The theory was first proposed by Helmholtz⁴⁹ in 1879 and subsequently modified by a number of workers, among them Gouy, Chapman, and Stern, with latter's theory being more generally accepted⁴⁹. In its simplest form the theory states that hydrophobic particles (e.g. clays, hydrous metal oxides, bacteria) suspended in water carry electrical charges at their surfaces, and surface charge density (σ) remains constant with size variation. The charge carried by colloidal particles varies considerably in magnitude with the nature of the colloidal material and may be positive or negative depending upon the pH and ionic content of the aqueous phase. Colloidal particles in nature are mostly

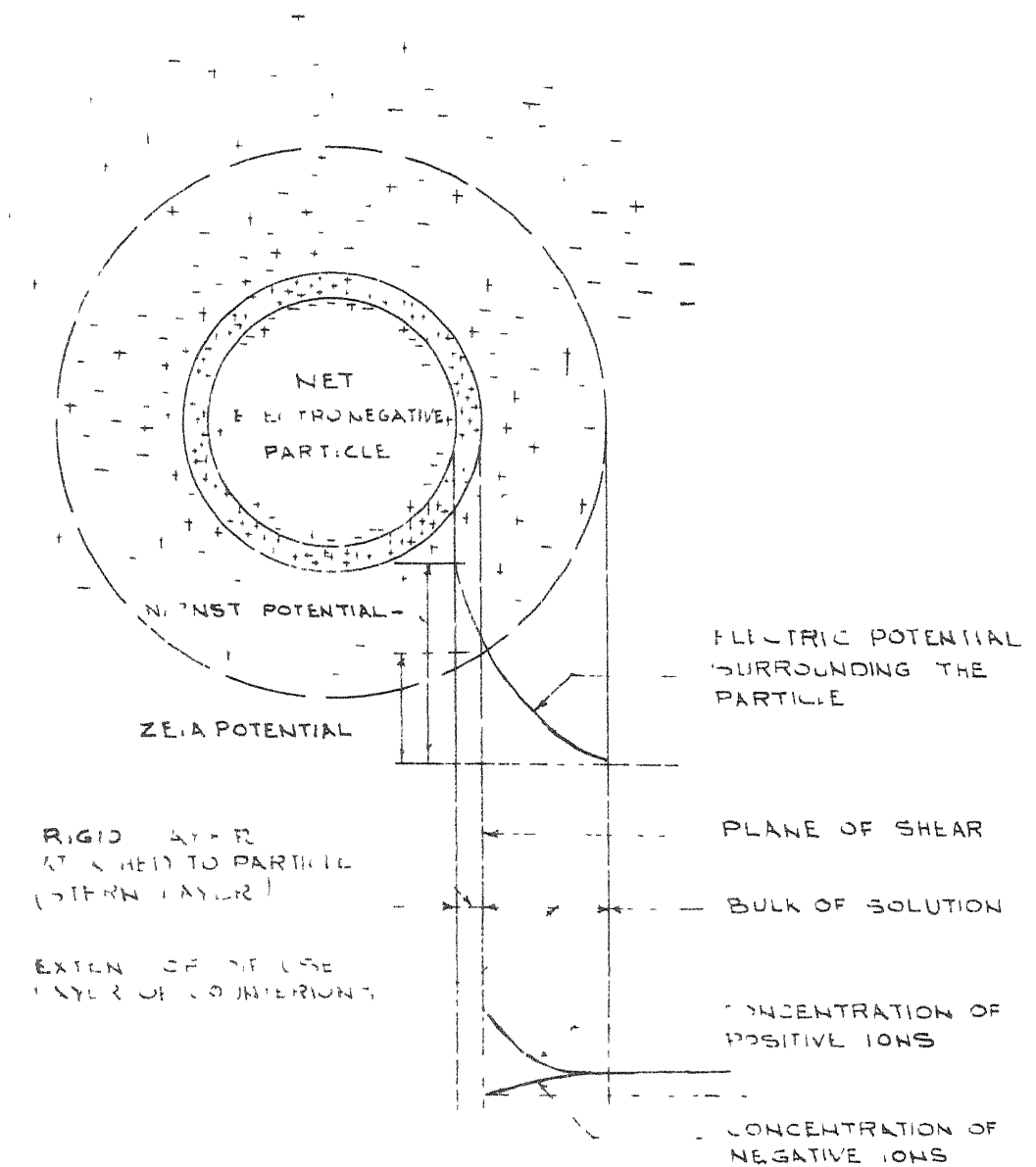
electronegative. These electrical charges may arise through direct ionization of one of its constituents (atoms at the particle surface), by replacement of elements in a crystal lattice by elements having different charge, or particles may acquire the charge through adsorption of ions from the water itself. Thus three mechanisms believed to be responsible for charge on clay mineral surfaces, are isomorphous replacement, broken bonds, and lattice defects^{28,36}.

In most instances charge is believed to be due to the preferential adsorption of $(OH)^-$ ions from the bulk of suspending water³⁸. The negative charge on a clay particle is probably due to firm attachment of hydroxyl or other anions from water which probably fit better into the lattice structure of the colloid, or more adaptable to the colloid than positive ions, which are often larger than negative ions. The tendency of anions to be adsorbed more than cations is also attributed to polarisation and mobility. Cations are most mobile¹⁹. The ions will be held at the surface when the binding energy (E) is large as compared to the thermal energy of the ion ($E \gg kT$). The binding energy E is dependent on size, hydration, charge, polarisability of the ion, dielectric constant. Anions are usually less hydrated and are more polarisable than cations owing to their large number of electrons per nuclear charge^{12,51}. Above reasons are thought to be responsible for greater adsorption of anions at interfaces. Colloids that acquire their

charge by ionization of some constituents usually behave like weak acids or bases. Their ionization and with it, their charge are elevated or depressed by the addition of H^+ or OH^- ions, and double layer ions are formed.

2.3A REPULSIVE FORCES

A colloidal dispersion (the solid and aqueous phases together) does not have a net electrical charge. To maintain electroneutrality the primary charge on the particle is counter-balanced by an electrical double layer at every interface between a solid and water. This double layer consists of the charged particles and an equivalent excess of the ions of opposite charge (counter-ions) which are attracted electrostatically to this interfacial region and are held in the liquid phase side near the surface of the particle³⁶. The detailed illustrative picture is given by Fig. 2.3.1. Oppositely charged ions arrange themselves in a diffuse second layer about the first layer. Thus there is a balance between the electrical forces which tend to attract counter-ions and repel co-ions, and thermal motion which tends to produce a uniform distribution of these ions, and prevents the formation of a compact electrical double layer. Thus diffused electrical double layer, often referred to as Gouy Chapman Double layer, is created due to combined effect of electrical forces and thermal agitation. Two competing process (diffusion and electrostatic attraction) spread the charge in diffuse layer, within which the excess



CONCEPT OF THE ZETA POTENTIAL

Fig. 2.3.1

concentration of counter-ions is highest adjacent to the surface of the particle and decreases gradually with increasing distance from the solid-water interface and eventually becomes zero where equal concentrations of cations and anions are present. The distinct charge of the colloidal particle is determined by the layer nearest to it. The net effect of the existence of electrical double layers around particles is to inhibit the close approach of particles to each other, and hence the double layer confer stability to the suspension^{27,49}.

Due to existence of the primary charge, an electrostatic potential exists between the particle surface and the bulk of solution. The potential has a maximum value at the particle surface and decreases with the distance from the surface. This decrease with distance is affected by the characteristics of the diffuse layer, and thus by number and type of ions in bulk solution. Depending upon the origin of the primary charge, the surface potential may also decrease with increasing ionic strength. At some distance from the particle and within the diffuse layer there exists a plane of shear representing the portion of bound water and ions that will remain attached to the particle as it moves through the suspending liquid. The potential at the surface of the particle, also called the 'total potential' or Nerst Potential⁴⁹; is represented by $\psi(\text{psi})$. At the plane of shear (bound-water layer) 'Zeta potential' is located. (Nerst Potential-Stern Potential = Effective Potential or Z.P.). Zeta potential of the colloidal

particle is the measure of the electrostatic repulsion. Approximate value of zeta potential is obtainable from easily measured electrophoretic mobilities.

$$\text{Z.P.} = \frac{4\pi dQ}{D} = \frac{4\pi\mu M}{D}$$

(M for water is 0.8 to 1.3 microns/sec/Volt/cm)

The zeta potential is thus a measure of both of the charge on a colloidal particle and of distance into the solution to which the effect of charge extends. While discussing the Z.P. and charge density at a flat or spherical surface, significance is attached to a/d . When (a/d) is small, the particle is considered as a point charge, when it is large, the double layer is almost flat. Following equations of Huckel and Smoluchowsky hold within one percent for $a/d < 0.5$ and $a/d > 300$ respectively:

Huckel's Equation¹² $Q = (\text{ZP})(1 + a/d)Da$ where $Q = 6\pi\eta aM$

$$M = D(\text{ZP})/6\pi\eta \quad \text{and} \quad (a/d) < 0.5$$

Smoluchowsky's Equation¹² $M = (\text{ZP}) \frac{D}{4\pi\mu}$ for $(a/d) > 300$

Unfortunately sanitary engineer's field of interest lies between these values. Though Henry attempted to put forth an equation for general application for any value of (a/d) , but his equation is based on several simplifying assumption and these limit the validity of calculated zeta potential.

Henry's Equation¹² $M = \frac{D(ZP)}{6\pi\eta} f(a/d)$

$f(a/d)$ = Henry's function (varies from 1.0 for small values of a/d to 1.5 for large values of a/d).

It is believed³⁶ that raw water colloids can be destabilized, coagulated and removed effectively only by changing the Z.P. of both the floc and the colloid to the value of approximately zero or ± 5 mV at the optimum pH⁴⁸. Elwood⁴⁷, L.B. et. al. reported that optimum turbidity removal requires somewhat negative Z.P. out to be in the range of -4 to -7 mV.

On the basis of such findings hope was entertained that complex art of water treatment finally could be reduced to an exact science by direct measuring a single parameter M or ZP to predict correct dosage of coagulant for best coagulation. However, the consideration relating to electrokinetic behaviour and stability relate only to purely hydrophobic colloids. Hydrophobic colloids by definition soluble at their isoelectric point also, and, therefore, may not be coagulable over any and all ranges of M or ZP¹².

2.3E ATTRACTIVE FORCES

Certain attractive forces also exist between all types of colloidal particles, no matter how dissimilar their chemical nature may be. Those attractive forces, termed as London Van der Waal's forces, are responsible for the aggregation of many colloidal systems. Their magnitude depends upon the

kinds of atoms which make up the colloidal the colloidal particles and the density of the particles and essentially independent of the composition of the aqueous phase¹⁶

$$F = - \frac{3}{4} h \frac{\nu \alpha_1 \alpha_2}{r^6}$$

where h = Planck's constant

α_1 & α_2 = static polarization (mass) for particles
1 and 2

ν = frequency, and

r = clear spacing between two particles.

One of the factors generally cited as important to instability of colloid particles is Brownian movement. Very small solid particles, particularly those with particle diameters 100 millimicron or less, in a colloidal dispersion are in constant motion, and so they have kinetic energy. The energy for this motion of the particles is obtained from collisions with water molecules and is directly related to temperature, the energy increasing with increasing temperature. The particles are bombarded from all directions, resulting in a rapid and random movements of the colloids increasing the probability of particle collisions. These particle contacts will not, however, result in a sufficient number of lasting unions unless the colloids have already been destabilized. Moreover for larger particles, Brownian movement becomes a negligible factor.

Thus the effects of charge on the apparent stability of irreversible colloids may be determined by summing the repulsive and attractive energies of the interaction. The net interaction energy ($V_R - V_A$) is a function of the separating distance. The repulsion energy is an exponential function of the distance with a range of the order of the thickness of the double layer, and the attraction energy is ~~inversely~~ proportional to the sixth power of distances over small distances. Consequently, attraction predominates at very small and at large distances. At intermediate distances repulsion predominates depending upon the actual value of two forces i.e. net energy of interaction. The net repulsion acts as an energy barrier (refer to Fig. 2.3.2) which must be overcome for aggregation to occur; its magnitude depends upon the charge on the particles and the ionic composition of the solution. Therefore rate of coagulation is dependent upon the magnitude of the energy barrier and the kinetic energies of the particles. Irreversible colloidal systems which have a high activation energy and/or a low kinetic energy will coagulate very slowly while colloids with a low activation energy and/or a high kinetic energy will coagulate rapidly.

2.4 DESTABILIZATION OF COLLOIDS

As discussed in previous section 2.3 factors tending to destabilize colloids are gravitational forces, Van der Waals forces, and Brownian movement. Gravitational force, due to

REPELSION

ATTRACTION

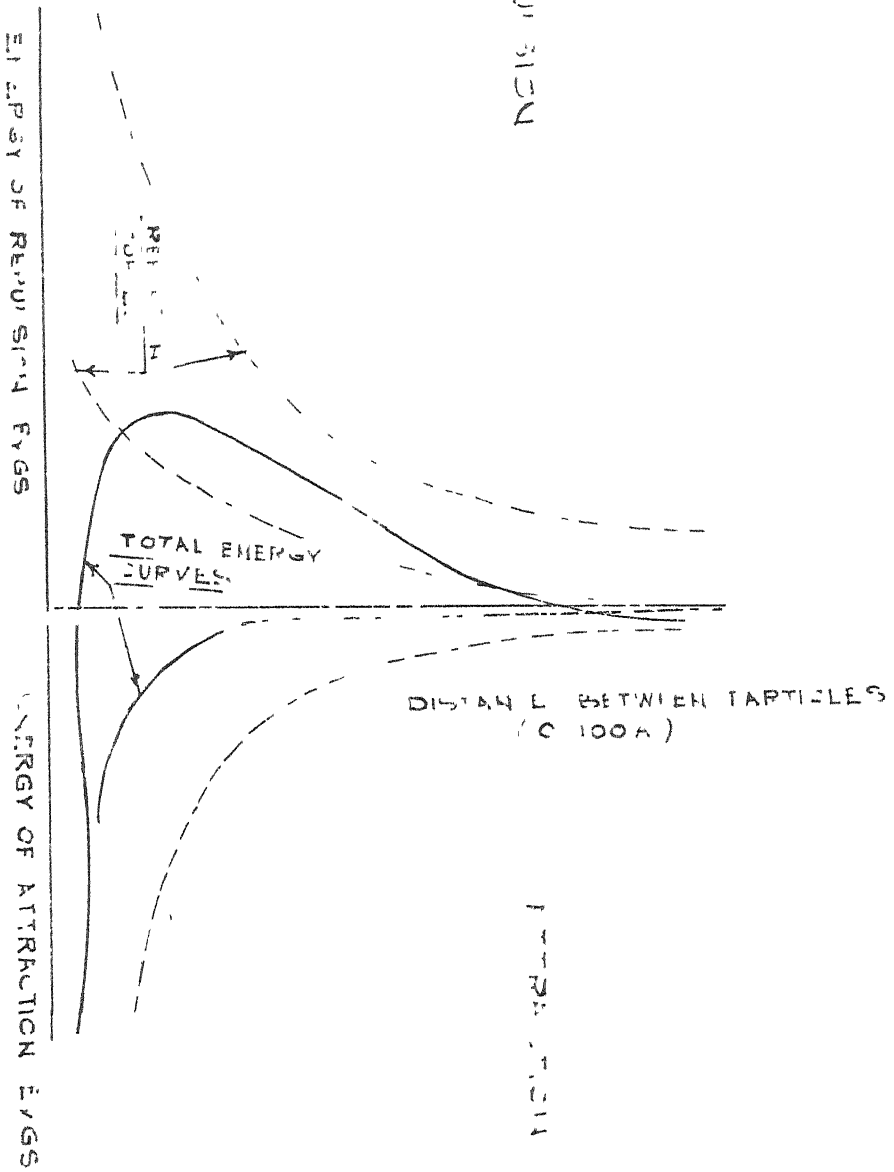


Fig 2.3.2

small mass involved in colloidal systems, is relatively small compared to other system forces. Van der Waals forces ($\propto r^{-6}$) are negligible when masses are even slightly separated, they become dominant if physical contact is induced by mechanical or chemical means. Brownian diffusion, a random motion of the colloidal particles, is as a result of the impact with molecules of the suspending medium. Molecule has to cross energy hump for collision to take place, as shown in Fig. 2.3.2.

2.4A AGGREGATION OF HYDROPHOBIC COLLOIDS

The aggregation of hydrophobic colloids may be accomplished in four major ways³⁸:

(1) Boiling, (2) Freezing, (3) Addition of electrolytes, and (4) Mutual precipitation by addition of colloids of opposite charge.

1. Boiling - raising the thermal energy is not a practical and economical proposition.
2. Freezing - During the freezing process, crystals of relatively pure water form. Thus the colloidal and crystalloidal materials are forced into a more and more concentrated condition.

The commonest method of turbidity removal in sanitary engineering is by addition of metal coagulants and polyelectrolytes

During the 1880's the classical colloid chemists observed that monodisperse colloidal sols of high concentrations could be coagulated by addition of electrolytes. Schultze in

1882 and Hardy in 1900 studied these reactions and summarized their studies as Schultze-Hardy rule, discussed earlier signifying the relation between ionic charge and precipitating power of electrolytes. Derjaquin and Verwey in 1940 and 1941 and Overbeek in 1948 placed the above reactions on a quantitative basis essentially confirming the Schultze-Hardy rule of valency dependence⁴⁹.

2.4B ALUM COAGULATION

Coagulation process using aluminum and iron salts as coagulants is ancient and has been in continuous use for the past 100 years to the present, but knowledge of the precise behavior has generally been lacking. Even though Mattson⁴⁷, as early as 1929 had pointed out that hydrolysis products of aluminium and ferric salts were more effective in coagulation than the ions themselves, his work was largely ignored by the water-treatment field. Theories based on tripositive metal ions continued to be expressed as late as the early 1960's.

In 1948 Black⁹ attempted to summarize the existing theory, as to mechanism of coagulation, in three steps:

- (1) Neutralization of negative charge by tripositive alum ions (the amount and type of which are the function of the water pH).

- (2) Agglomeration and growth of small flocs by slow stirring, and

(3) Surface adsorption or entrappment of particles on the large surface area of the floc particles.

Camp, Root and Bhoota¹⁵ hypothesized that the formation of the floc takes place in following steps:

(A) Formation of the precipitate as a result of chemical reaction,

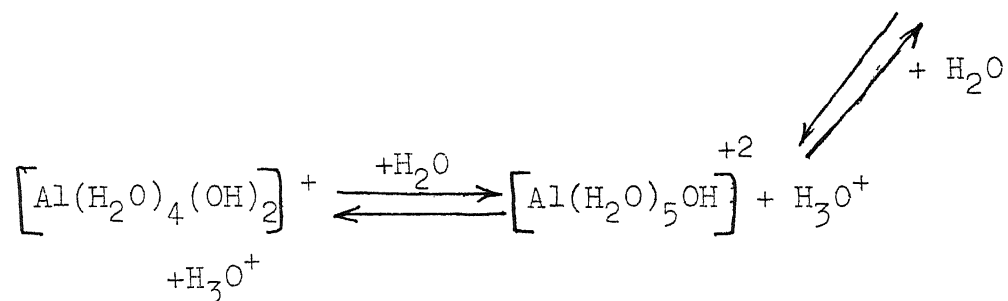
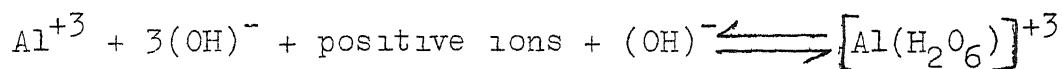
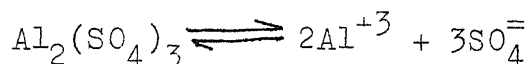
(B) Formation of floc by Brownian motion, and

(C) Final floc growth as a result of velocity gradients.

It was concluded from their experimental results that Brownian Motion phase i.e. perikinetic coagulation was probably near completion in 6 to 10 secs.

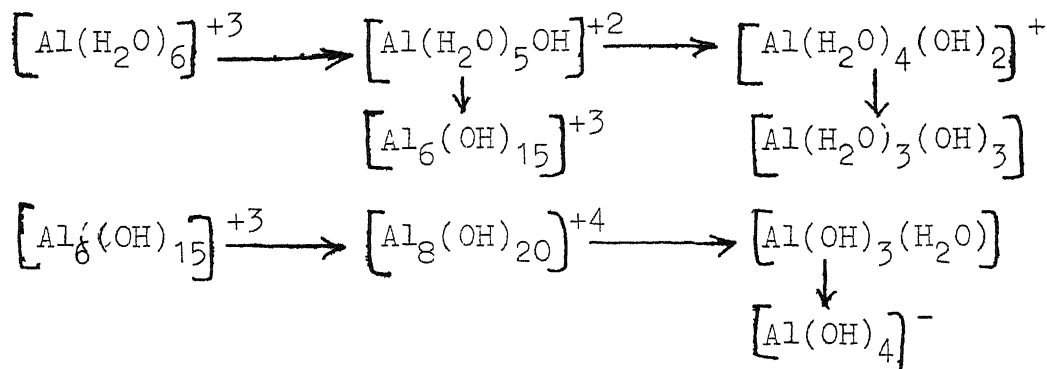
2.4C HYDROLYSIS OF ALUMINUM SALTS^{51,49,12}

All metal cations are hydrated in water solution. These aquometal ions are proton donors (acidic). The currently held view, supported by theoretical and experimental evidence, is that aluminium ions, almost instantly after addition to water, enter into a series of hydrolytic reactions with water to form a series of multivalent charged colloidal, hydroxo, metal polymeric ions, as intermediates in the formation of the metal hydroxide precipitates. Depending upon pH, these compounds may range from positive at the lower pH values to negative at the more basic pH values. These reactions can be represented as follows:

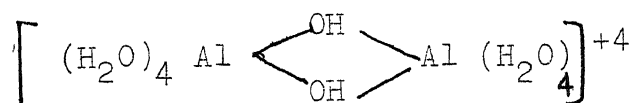


This reaction can proceed until the neutral species

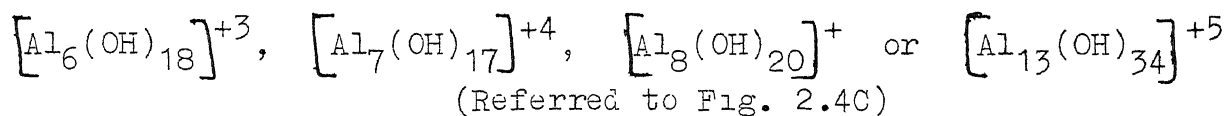
$\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ or a negatively charged species $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ are formed.



Recent¹² evidences also indicate that monomeric species (containing only one aluminium ion) are at best transient and olation-polymerisation reaction involving several ions (metal ions) bridged by hydroxyl group takes place and simplest reaction leading to dimeric species can be:



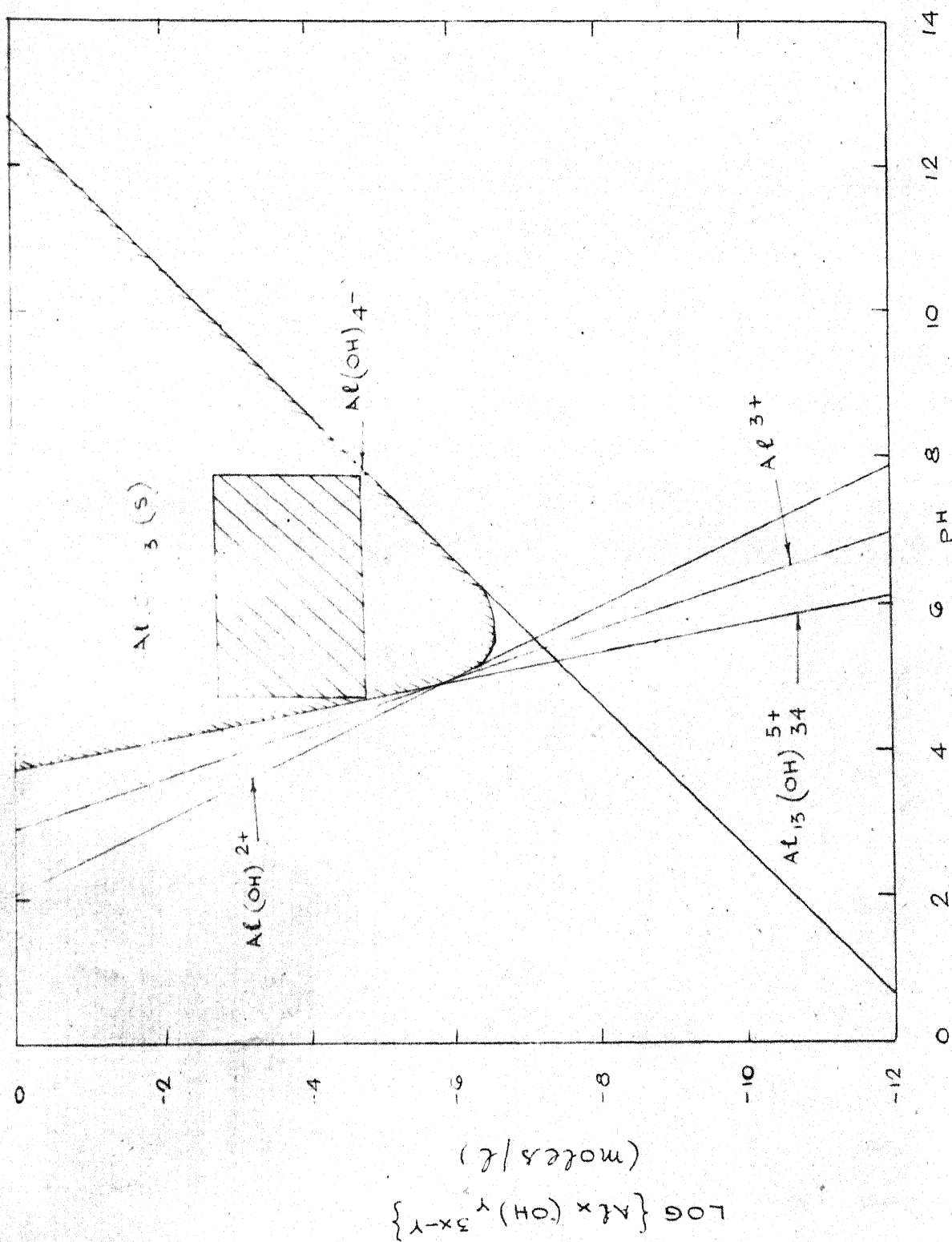
It is the intermediate soluble, hydro, metal ions that coagulate or destabilize turbidity colloids in water. It is believed that effective hydrolysis products for coagulation are of the types:



Due to chemical conditions a mixture of these compounds is formed. But at low concentrations of aluminum most important complex is a polynuclear $[Al_8(OH)_{20}]^{+4}$. In keeping with Schultze-Hardy rule, the most effective coagulant will be the mixture with the highest positive valence. Which hydroxometal ion will predominate is a function of the pH^{12,49}.

The hydroxide ion is only one of the ligands which can enter into the chemical structure of the coagulant ion. Other basic ions such as carboxyl, phosphate, sulfates, chloride, etc. may also form complexes. The chemical structure of the various hydrolysis products determine their electrical charge and the chemical structure is determined by the coagulant, the solution composition and pH of the reaction. The concentration of soluble Al^{+3} and Fe^{+3} in water at pH7 are about 30 micron g/l and 5.6×10^{-7} micron g/l respectively indicating that soluble species are less significant in the destabilization of the colloids³⁴.

O'Melia and Stumm⁵¹ have also concluded from their studies that destabilization of colloidal dispersion is



SOLUBILITY EQUILIBRIA OF AMORPHOUS $\text{Al(OH)}_3(\text{s})$
 Al(III) EQUILIBRIA

Fig: 2.4.C

accomplished by the soluble, polymeric, kinetic, intermediates, which are formed in over saturated solutions during transition to the precipitation of the metal hydroxide. They proposed stoichiometric relationship (a direct linear proportionality) between coagulant dosage and surface area of the colloid. But Packham⁵¹ has demonstrated that an increase in turbidity of natural waters causes decrease in coagulant dosage for destabilization. O'Melia and Stumm offered a possible explanation for this abnormal behavior that at low concentrations (i.e. low turbidity) a large excess of metal coagulant addition produces a voluminous precipitate of metal hydroxide which enmeshes colloidal particles as it precipitates. They have also opined that an over-emphasis on electrostatic phenomena in studies of coagulation in natural systems can produce results that are in-effective, uneconomical or both.

2.4D DESTABILIZATION BY POLYELECTROLYTES^{49,26}

Synthetic polyelectrolytes (consisting of linear chain of hundreds of carbon atoms linked together in repetitive fashion) are made from a variety of monomers (ampholytic - containing both positive and negative groups) and are broadly classified on the basis of their electric charges as (a) Anionic (-), (b) Cationic (+) and (c) Non-ionic (no charge)⁴⁹.

Both anionic and cationic polyelectrolytes produce exceptionally heavy floc depending upon solution characteristics of the system, like pH, concentration of divalent cations

Ca^{++} , Mg^{++} , etc.²⁶.

The polyelectrolytes having linear thread like colloids have like charges (recurring throughout the length of the molecule. Due to repulsion colloid exists in the water stretched out for its length. Any colloidal impurity having an opposite charge would be certain to be entrapped even though charge is mildly evident⁴⁹.

The anionic polyelectrolytes (negatively charged upon ionization as typified by polyacrylamides or polycarboxylic acids) are powerful coagulants for dispersions stabilized by positive charges. In addition, an ionic polyelectrolytes are also employed for improvement of the properties of the flocs formed by addition of aluminum or iron salts. Tests have shown that the effectiveness of anionic polyelectrolytes is nearly independent of pH, alkalinity, hardness, and turbidity. However, the optimum dose of polyelectrolyte increases linearly with alum dosage.

The cationic-polyelectrolytes (as typified by polyamines are positively charged upon ionization).on the other hand have the ability to act both as coagulant and a coagulant-aid, since in general, the charge involved would be opposite to each other.

The polymers are believed to provide charged nuclei inducing aggregation of microflocs. The desired result is a tough floc, resistant to attrition and easily dewatered.

2.5 MECHANISM OF DESTABILIZATION:

Aggregation of colloids is considered as involving two steps (1) Particle transport to effect interparticle contact, and (2) Particles destabilization to permit attachment when contact occurs.

The coagulation is concerned with origin and nature of stabilizing forces discussed earlier in Section 2.3 within the sols, and the effects of addition of polyelectrolytes, coagulants, coagulant-aids in lessening stability.

The second aspect, flocculation is the process of aggregation of sub-visual floccules into larger, rapidly settleable flocs once instability has been attained.

Thus flocs growth is mainly dependent upon two factors - collision which in turn depends entirely upon physical action, particularly agitation of water and adhesion which is controlled by chemical or electronic forces.

By reviewing the existing explanations, possible mechanisms for destabilization of colloids may be summarized⁵¹ as follows:

1. Compression of double layer
2. Adsorption to produce charge neutralization
3. Enmeshment in a precipitate; and
4. Adsorption to permit interparticle bridging

(1) Destabilization by counter-ions is accomplished by compressing the diffuse layer surrounding the colloidal

particles. High concentration of electrolyte in solution results in correspondingly high concentration of counter-ions in the diffuse layer. The volume of the diffuse layer necessary to maintain electroneutrality is lowered and consequently the thickness of the diffuse layer is reduced. The range of repulsive interaction between similar colloidal particles decreases and the activation energy barrier disappears.

(2) The ability of a coagulant to destabilize a colloidal dispersion is actually composite of coagulant-colloid, coagulant-solvent, and colloid-solvent interactions. Matzlevic, Janaver, and Kerker⁵¹, (1964) have shown that coagulation with Aluminum salts is effective at low dosages (4 mg/l of alum). Second restabilization occurs at higher dosages (25 mg/l) of alum and is accompanied by charge reversal. Finally, coagulation is again observed at still higher dosages. They have concluded that initial destabilization and the subsequent restabilization are brought about by adsorption of Al (III) species from the solution. The second area of coagulation at higher Al (III) dosages is brought about by enmeshment of the colloidal particles in a precipitate of aluminum hydroxide. Refer to Fig. 2.4.C.

(3) When $Al_2(SO_4)_3$ is used in concentrations sufficiently high to cause precipitation of aluminium hydroxide, colloidal particles are enmeshed in these precipitates as they are formed

Several mechanisms for increasing the efficiency of these collisions (destabilizing the particles) have already been discussed in previous sections. Size of the treatment facilities provided to achieve a desired efficiency of aggregation of these particles; is dependent upon aggregation rate. The flocculation/aggregation rate is measured by determining the decrease of the number of particles by one-half after certain interval of time (flocculation time $t_{1/2}$).

Present understanding of particle transport in coagulation processes is based on the work of Smoluchowsky (1917). Smoluchowsky¹⁰ developed a theory of rapid flocculation, applicable to a situation where every encounter between the particles leads to a permanent contact. The application of Smoluchowsky theories to the design of flocculation basins has been developed by a number of authors (Camp & Stein, 1943; Camp, 1955; Hudson, 1965; Hudson and Wolfner, 1967).

For interparticle contacts, like particle destabilization, can be accomplished by three separate mechanisms:

- (1) Contacts by thermal motion/diffusion - perkinetic flocculation.
- (2) Contacts resulting from bulk fluid motion - transport induced by stirring-orthokinetic flocculation, and
- (3) Contacts resulting from the differential settling of the particles - 'handered settlement'.

If flocculation is assumed to be entirely diffusion controlled, then for monodispersed colloids⁵¹ the rate of change in total concentration of the particles with time shall be as follows:

(Packham⁵¹, 1965)
$$\frac{[Al^{+3}][OH^{-}]^3}{K_3} > 100 \text{ or higher for rapid precipitation conditions}$$

when precipitate is positively charged and pH of the solution is in the neutral range, the rate of precipitation is also increased by the presence of anions ($SO_4^{=}$) in solution. Finally, the colloidal particles themselves serving as nuclei for the formation of precipitate increase precipitation rate. In other words an inverse relationship develops between optimum coagulant dosage and the concentration of colloidal particles to be removed.

(4) Adsorption and interparticle bridging - It is often observed that the most economical treatment is obtained with an anionic polymer, even though colloids are negatively charged. La Mer and coworkers⁴⁹ developed a bridging theory - a polymer molecule containing chemical groups which interact with the sites on the colloidal particle surface. These active groups are adsorbed at the particle surface, leaving other vacant adsorption sites for other particles. A particle-polymer-particle complex is thus formed in which the polymer serves as a bridge.

It is not known what relative importance the two mechanisms electrostatic adsorption and enmeshment, have in any coagulation and flocculation system, but undoubtedly both play significant roles.

2.6 GROWTH OF FLOCS:

The rate of aggregation of colloidal particles is determined at which collisions occur between particles (particle transport) and by effectiveness of these collisions in permitting attachment between colliding particles (particle destabilization).

Because of the significant difference in physical mechanisms causing flocculation, the flocculation kinetics is divided in two parts viz. Perikinetic and Orthokinetic. In the first phase, perikinetic flocculation Brownian motion is the principal agent causing close approach or collision of colloids. The rate is function of the net repulsive or attractive force between and the bridging action of the polymeric molecules attached to the particle surface.

In the second orthokinetic flocculation, the approach results primarily from fluid velocity differences and lesser dependence exists on particle size and other surface properties.

Orthokinetic flocculation is effective for long times. Brownian motion is more effective in flocculating very small particles while larger ones are most affected by induced velocity gradients. To ascertain extent all the particles are subjected to flocculation by both the mechanisms. Their relative effectiveness in promoting flocculation being related to particle size of the suspension, and to a lesser extent to temperature, and to energy dissipated in creating velocity gradients.

2.6.1 Destabilization By Perikinetic Flocculation.

$$J_{PK} = \frac{dN_0}{dt} = - \frac{4\pi kT}{3\mu} (N_0)^2 \quad (\text{Swift \& Friedlander, 1964})$$

($k = 1.38 \times 10^{-6}$)

$$N^o = N_o^o \text{ at } t = 0, \quad t_{1/2} = \frac{3\mu}{(4 \eta kT N_o^o)}$$

$$\text{or, } N_o = \frac{N_o^o}{1 + \left(\frac{4 \eta kT N_o^o}{3\mu}\right)t} \quad \text{or } N_o = \frac{N_o^o}{1 + t/t_{1/2}}$$

under these assumptions $t_{1/2}$ is seen to depend on the initial particle concentration and collision efficiency.

Smoluchowsky theory has been found to hold reasonably well for the flocculation of a number of sols in the presence of sufficient electrolyte to remove the potential energy maximum. For fast flocculation (where each collision results in aggregation of which usually occurs of sufficiently high concentration of electrolyte is present).

$$N^o = N_o^o / 1 + (t/t_{1/2})$$

while for slow flocculation (due to low electrolyte concentration, each collision does not necessarily produce agglomeration), the time $t_{1/2}$ will be longer.

$$N^o = \frac{N_o^o}{1 + \left(\frac{t}{t_{1/2}}\right)}$$

2.6.2 Destabilization By Orthokinetic Flocculation.

In many cases it is observed that fluid motion or agitation accelerates the interparticle contacts/aggregation. In such systems the fluid velocity varies both spatially (from point to point) and temporally (from time to time). These velocity differences or gradients in the water which cause

contacts also cause shearing stresses along planes in the water, and to overcome these power is needed⁴⁶.

$$\Omega = \left(\frac{\pi d_o^3}{6} N_o \right) \ln \frac{N_o}{N_o} = -\frac{4}{\pi} \eta \Omega G t$$

$$\text{For monodispersion } J_{OK} = \frac{dN_o}{dt} = \frac{-2 \eta G d^3 (N_o)^2}{3} = -\frac{4 \eta}{\pi} G \Omega N_o$$

$$\text{ratio } \frac{J_{OK}}{J_{PK}} = \frac{-2 \eta G d^3 (N_o)^2 / 3}{-4 \eta kT (N_o)^2 / 3 \mu}$$

$$\frac{J_{OK}}{J_{PK}} = \frac{\mu G d^3}{2kT}$$

The rate of orthokinetic flocculation is seem to be first order w.r.t. to concentration of particles, the velocity gradient, and the floc volume fraction. At 25°C in water-colloids systems, to keep ratio unity particles should have following velocity gradients:

$$\phi 10 \quad - 0.01/\text{sec}; \quad \phi 1 \quad - 10/\text{sec}; \quad \phi 0.1 \quad - 10,000/\text{sec}$$

The velocity gradients on the order of 10 to 100/sec are quite common. Stirring, therefore, will not enhance the aggregation rate of small particles until they grow to a size of about 1 μ , but 1 μ particles do not settle well. Particle growth to a size larger than 1 μ requires fluid motion by agitation or other means.

Interparticle contacts are frequently achieved by mechanically stirring with rotary paddles. The mean velocity gradient in any system shall depend upon the power which is dissipated within water.

$$G = \left(\frac{P}{V\mu} \right)^{1/2} \quad (\text{Camp \& Stein}^2, 1943)$$

where $G = \left(\frac{\text{mean value of dissipation function}}{2\mu} \right)^{1/2}$

and $F_D = C_D A \int_1 \frac{v_r^2}{2} \quad (\text{Camp, 1955})$

Power required to overcome the drag of a single rotating blade

$$W = 0.97 C_D A v^3.$$

$$P = F_D V_f \quad \text{and} \quad G = \left(\frac{C_D A \int_1 v_r^3}{2\mu V} \right)^{1/2}$$

Considerable difficulties are encountered in evaluating v_r (the relative velocity of paddle w.r.t. fluid), it is estimated that v_r varies from 0.5 to 0.75 for paddle flocculators.

The performance of the flocculation unit is in large measure determined by its effectiveness in promoting orthokinetic flocculation by stirring induced velocity gradients as the mixing of the chemicals and perikinetic flocculation by Brownian motion are rapidly accomplished.

Design of flocculation unit involves the selection of a velocity gradient, a reactor configuration, and a detention time sufficient to produce aggregation of a size suitable for removal in a subsequent treatment unit. Of greater importance such as η and Ω are almost impossible to measure in the field and even G can be measured with only great difficulty⁵¹.

The detention time is inversely proportion to collision efficiency factor. Very little information is available concerning the magnitude of η in field operations. Certain laboratory data⁵¹ is available. The η will depend upon the

colloids to be treated and other chemical characteristics of the solution as well as the coagulant which is used. Hahn¹⁹ and Stumm⁴³ (1968) report that η is unaffected by the type of flocculation which occurs (perikinetic versus orthokinetic) when Al (III) salts are used as coagulants.

The effectiveness of flocculation facilities has been considered by Camp⁵¹ to be proportional to the product of the velocity gradient (per sec.) and the detention time, T (secs), Gt. He found that G varied from 35 to 66 sec⁻¹ in existing plants where paddle wheels were in use, and with values of Gt from 48,000 to 210,000. In baffled basins the values varied from 20 to 74 and 23,000 to 121,000. It is believed that in both types values of G should be not less than 10 and not more than 75 sec⁻¹, with optimum values between 25 and 65. Weber (1971) reports that in water treatment systems providing acceptable coagulation the dimensionless product ($\eta \Omega Gt$) is probably in the order of 0.1 ($G = 10/\text{sec}$, $t = 10^3 \text{ sec}$, $\Omega = 10^{-4}$, $\eta = 10^{-1}$).

Peripheral speeds of the paddle wheel range in practice from 0.6 to 2.5 ft/sec. Usually the velocity of the water will be about one-fourth the blade velocity; i.e., the velocity differential will be 0.75. Normally paddle area should not exceed 15 to 20 percent of the cross-sectional area of the basin, or rolling of water may result, without necessary velocity gradients. Normally following values⁵¹ are used in practice:

$$G = 20 \text{ to } 30 \text{ sec}^{-1}$$

$$Gt = 30,000 \text{ to } 40,000$$

$$t = 15 \text{ to } 45 \text{ mts or } 900 \text{ to } 2700 \text{ secs.}$$

2.7 FACTORS INFLUENCING COAGULATION & FLOCCULATION

As discussed in Sec. 2.1 to 2.6, the following factors will be the more significant ones to influence the effectiveness of coagulation process:

- (1) Amount and Character of Turbidity
 - Size and zeta potential of the colloidal particle
 - Concentration and cation exchange capacity of colloidal suspension
- (2) Total Alkalinity of Water
- (3) pH: Hydrogen Ion Concentration of Water
- (4) Type and Quantity of Coagulant
- (5) Type and Quantity of Coagulant aids (auxillary-chemicals),
Presence of Nuclei
- (6) Other Chemical Characteristics of Water
 - a. Monovalent cations Na^+ , K^+
 - b. Monovalent anions Cl^- , NO_3^-
 - c. Divalent cations Ca^{++} , Mg^{++}
 - d. Divalent anions $\text{SO}_4^{=}$
 - e. Color, Hardness (salt concentration)
- (7) Rapid Mixing
- (8) Speed of Paddles - Velocity Gradient in Flocculation Chamber
- (9) Flocculation Time
- (10) Water Temperature

2.7.1 Amount and Character of Turbidity:

As described earlier, in section 2.1 turbidity in surface waters consists largely of clay and other mineral particles e.g. Kaolinite, Illite, and montmerillonite. The size range of most of these particles is about 0.2 to 5.0 which places them in upper size range of the true colloids and in a size range, which would settle under gravity, if sufficient detention time is given¹⁷. In 1952, Landiev⁴³ observed that clay particles smaller than one micron in diameter gave rise to a good floc. Particles larger than 5 were found to have little effect on coagulation. The dose of coagulant required to bring about coagulation increased slightly as the particle size decreased.

A broad distribution of clay particle sizes is much easier to coagulate than a suspension containing single or narrow range of particle sizes⁵⁰. Rao³⁴, Deshpande⁴⁷, et. al. found that effect of increasing the concentration of suspended clay was a gradual reduction of the dose required to halve the turbidity. This indicates a major difference between the behaviour of dilute and more concentrated suspensions. It is concluded that coagulation of dilute suspensions is controlled more by the coagulant and the composition of the water than by the nature of suspended solids being removed. Paradoxically, with very high turbidities relatively smaller coagulant doses are required because of the high collision probabilities, for

the same reason very low turbidities are frequently more difficult to coagulate. Thus the negative charge on the clay does not appear to be the only factor governing the stability of dilute suspensions. The easy coagulation of more concentrated suspensions may also partly be due to entry of hydrogen ions into the electrical double layers of the clay particles. In dilute suspensions, the interparticle distance will be more which lowers the probability of collision and reduces the rate of flocculation³⁶. The opportunity to collide is also related to three physical factors: (1) the size of the particles; (2) the number i.e. concentration of the particles; and (3) the relative particle movement. The importance of base exchange capacity, (the quantitative expression of the ability of clays to exchange cations, i.e. calcium for sodium, etc.) of suspensions had been emphasized in the earlier work of Langmuir and Ludevig⁴³, who had called attention to the importance of the particle size distribution and the binder action of the hydrolysis product of the metallic coagulants. The adsorption of clay would depend some what upon the type and amount of impurities.

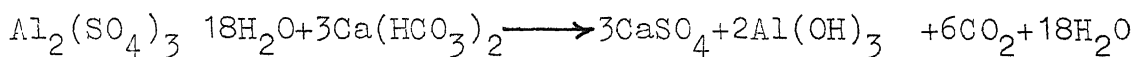
Riddick³⁶ reported that raw-water colloids can be effectively removed only by lowering the zeta potential of both floc and colloid to a value of approximately zero, plus or minus about 5 mV.

In accordance with the above amount and characteristics of suspended matter are important for coagulation.

2.7.2 Alkalinity:

The carbonates and bicarbonates of calcium, sodium, and magnesium are the common salts that cause alkalinity of most waters. Enough alkalinity must be present in the water to neutralize the acidity produced by hydrolysis of the coagulant, because the rapidity of hydrolysis process depends upon the amount of alkalinity¹. Since alkalinity adds ions to the solutions it may change the charge on the colloids present. Alkalinity increases the negative charge on the negative colloids present in natural waters¹⁰.

1 g.p.g. (17.1 mg/l) of alum theoretically requires only about 8 mg/l (7.2 ppm exact) of natural alkalinity. According to stoichiometry for each 100 mg/l alum added there should be 0.474 mg mol. reduction in alkalinity which is equivalent to 47.4 mg/l as CaCO_3 ⁴².



If alkalinity is expressed in terms of CaCO_3 , the theoretical requirement of 664 parts of alum works out to 300 parts of alkalinity i.e. approximately in the ratio of 2:1. Test results indicated that water demands about 54% alkalinity in relation to the alum injected. It has been reported by Babbitt, Doland et. al³⁴ that in general water requires 46 to 58% alkalinity concentration in relation to alum dose. But as experience indicates that better coagulation will be attained if 10 or 12 mg/l is available. Sufficient alkalinity should

be maintained (by adding lime or sodium carbonate), considering alkalinity reduction, for best coagulation. The dosage of the coagulant should be such as to provide a residual alkalinity of 5 to 10 ppm. Excessive alkalinity may, however, interfere with coagulation ultimately causing poor coagulation¹⁰.

2.7.3 Hydrogen Ion Concentration; pH:

It is generally agreed that the pH is of the greatest importance in the overall coagulation system. There is a pH zone of optimum coagulation for each natural waters in which destabilization occurs in the shortest possible time with minimum coagulant concentration. Cation exchange capacity of colloidal particles also vary considerably with pH. The chemical composition of waters has a considerable influence on the optimum pH range for various coagulants. The experience of waterwork chemists^{18,50} is that coagulation is most efficient in neutral pH range: 6.5 to 8.5, (for moderately hard waters 150 ppm) depending upon chemical characteristics of water, where Al(III) residuals are low, thus $\text{Al}(\text{OH})_3$ as active coagulant. Outside the optimum pH range coagulation is less effective and therefore most costly. The optimum pH range for alum coagulation is 4.0 to 7.0⁴⁸.

Above effects are because the pH interaction with the charge of the particle, which can be determined by electrophoretic techniques when the resulting charge on the floc particles may be either due to adsorption of H^+ ion or OH^- ion

at given pH value³⁶.

The stability of any aluminum hydroxidation species is pH dependent, but it is uncertain which specific form is stable at a specified pH. Matjevic et. al.⁵¹ suggests that most probable species at pH 4 as hydrated trivalent aluminum ion and between pH 4 and 7 as tetravalent aluminum. Riddick³⁶ is of the opinion that since aluminum hydroxides are amphoteric, their Z.P. is readily changed by pH, with isoelectric points ranging from 5.9 for CP aluminum hydroxide to 7.1 for that electrolytically prepared³⁶. Anions generally interact with metal ions to extend or displace the optimum pH of coagulant to acid side.

Experimental evidences^{3,34} indicate that with a positive sol a decrease in pH would usually increase the amount of electrolytes necessary for coagulation and vice versa. With a negative sol, it is reported that an increase in pH would usually increase the amount of electrolyte necessary for flocculation and vice versa.

2.7.4 Type and Quantity of Coagulant:

The very essence of colloid stability¹⁹ is that the zeta potential (and therefore the colloid stability) of electrocratic colloids is a function of the valence, type, and concentration of the electrolyte. Effective coagulation requires proper dosage of the coagulant (depending upon turbidity of raw water) and auxillary chemicals, when needed, adequate

mixing and other suitable physicochemical conditions (pH, alkalinity, temperature, etc.) for subsidence¹⁶.

The Schultze-Hardy rule³⁸, signifying the relation between ionic charge and precipitating power of an electrolyte; states that precipitation of a colloid is affected by that of an added electrolyte which has a charge opposite in sign to that of colloidal particles and the effect of such ion increases markedly with the number of charges it carries. The flocculating power (hence zeta potential controlling) of bivalent ion is 20 to 80 times that of univalent and the flocculating power of trivalent ion is 10 to 100 times than that of bivalent ion. In practice, required coagulated dose is based upon the rapidity with which floc settles out. With alkalinity and pH favourable, the quantity of coagulant is the most important factor influencing the time required for good floc formation¹². Hudson¹⁹ based on his Jar Test studies concluded that at constant G, the volume of the floc was proportional to alum dose.

Commonest coagulants in practice are aluminium and ferrous sulfates, but alum is mainly used due to many advantages: cheap, reduces taste and color, floc formed is better and tough. Some studies¹⁷ done in past have shown that iron salts work better as coagulants than alum. Settling time, to give desired resultant turbidity, in case of iron salts floc is less than alum flocs. But compared to iron salts, less dose of alum is required for a percentage removal⁴⁷. An operator's finding⁵⁰ on turbidity removal indicate that alum dosage in

in grains per gallon shall be = $0.1360 (\text{Turbidity in JTU})^{1/2}$.

2.7.5 Type and Quantity of Auxillary Chemicals - Coagulant aids:

The formation of flocs, with such desirable characteristics as rapid settling and toughness is achieved by coagulant aids. The most widely used materials²⁰ may be: (1) Oxidants, (2) Adsorbants - weighting agents, (3) Activated silica, and (4) Polyelectrolytes. Common ones are polyelectrolytes and activated silica.

Activated silica is necessary for coagulation of many raw waters during certain seasons of the year when the natural silica content is low. Silica's function is to bend together and toughen the alum floc complex so that floc particles will build up during continuous agitation. This action is due to formation of a long chain inorganic polymer, and silica is unique in that it is about the only element normally present in raw water capable of long chain formation²⁷.

A major benefit obtained with polyelectrolytes is a very large increase in floc size resulting in greatly increased settling rate. Generally, cationic polyelectrolytes have moderately long chain lengths with molecular weight ranging upto about 25,000. Although they bind together and toughen the floc complex to a degree, cationics do not supplement silica in this respect. Depending upon the conditions of its use, such as pH and order of addition. (It is best applied about one minute after addition of the prime coagulant^{19,27}), activated

silica provides considerable benefits - increased rate of coagulation, reduced coagulant dosage, extended pH range of optimum coagulation, larger denser faster-settling flocs, more effective coagulation at low temperatures, improved color removal, and improved flocculation of high-turbidity waters⁴⁹.

2.7.6 Other Chemical Characteristics of Water^{20,10}.

In addition to the factors already discussed, there are other factors, discussed below, which are of importance in their effect upon the coagulation of water. The principal effect of certain ions is to alter - (1) pH range of optimum coagulation, (2) flocculation time, (3) critical coagulation concentration and critical stabilization concentration, and (4) residual coagulant.

(a) Monovalent cations Na^+ , K^+ - Higher the concentration of these ions, higher is the alum dose required and rate of coagulation is lowered. Saline waters cannot be coagulated easily.

(b) Divalent cations Ca^{++} , Mg^{++} - These are usually found in hard waters. Their concentration reduces the dose of alum required. Hard waters are easy to coagulate.

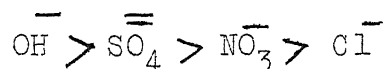
The zeta potential of the negative colloids is reduced by cations thereby reducing the repulsive force that holds the colloids.

Precipitating power of cations $\text{Al}^{+3} > \text{Ca}^{+2} > \text{Mg}^{+2} > \text{K}^{+1}$

(c) Monovalent anions - Cl^- , NO_3^- , These increase the alum dose and reduce rate of coagulation.

(d) Divalent anions - $\text{SO}_4^{=}$ slightly increases alum dose, but it improves the coagulation. The excess colloidal metallic hydroxides are neutralized by divalent $\text{SO}_4^{=}$ ions and thereby complete the coagulation of the colloidal system.

Stabilizing power of anions



Anions may also substitute hydroxyl ions in the polyhydroxy nuclear complexes, thereby forming different species. Substances carrying carboxyl or hydroxyl functional groups as well as inorganic phosphates, and to a minor extent even fluorides, chlorides and sulfates are able to coordinate with free metal ions. Complex bond anions may serve as bridges in the polynuclear network of hydrous precipitates and may lead to structures with varying extent of cross-linking^{12,51}. Black, et. al.^{9,10} have shown that the effect of sulfate is to broaden the range of good floc formation. It is clear that the presence of anions in solution would aid coagulation by attaching themselves to the positive colloidal material formed in the coagulation process. By the same reasoning cations such as sodium, calcium or magnesium should interfere with good floc formation. It may be concluded that in general anions interfere more with alum coagulation than cations. Anions extend the optimum pH range for coagulation to the acid region to an extent dependent on their valency.

2.7.7 Rapid Mixing:

Rapid mixing is the operation in water treatment, employed for express purpose of achieving complete homogenization of a coagulant chemical with the water to be treated, thus ensuring uniform reaction between applied chemical and the dissolved mineral constituents of the raw water. Inefficient mixing may have two harmful effects: (1) wastage of chemical, and (2) slower particle aggregation rate for a given chemical dosage²⁵. O'Melia, Hudson and Wolfner⁵¹ pointed out the necessity of rapid mixing based on reaction rate determinations made by Halm. Optimum turbidity removals were achieved when the coagulant was very rapidly and uniformly dispersed throughout the entire water body. In 1921, Langlier¹⁹ demonstrated the significance of agitation based upon the results of Jar Tests and a model three compartment continuous flow flocculator. He demonstrated an increase in rate of flocculation and a decrease in time required to produce satisfactory floc as the paddle speed was increased.

The design criteria suggest that the principal parameters of rapid mixing are intensity and duration. Rapid mix detention times of 30 to 60 secs are traditional with a minimum of 30 secs, at a mean velocity gradients from 300 to 350 sec^{-1} .^{46,51}

2.7.8A Speed of Paddles:

The fundamental purpose of mixing is not to build

up large floc quickly, but to secure a maximum number of impingements or collisions between the growing floc particles and the raw-water colloids. However, these collisions will result in permanent enmeshments of the colloid only if Z.P. is low³⁶. The velocity imparted to the water is usually two-thirds of the peripheral speed of the agitator blade. The Kauffman Equation²⁷ ($\log \frac{N_0^c}{N_0} = \frac{D a^3 G \phi V T}{\eta}$) shows that paddle speed in revolutions per minute will affect the magnitude of G. The higher the rotational speed of paddles, the more effective the coagulation. This is true upto a point. At any G, there is a maximum size of floc that can be formed. The floc will grow in size until shear forces set up by velocity gradients are equal to or greater than shear strength of the floc. Then, the particles of maximum size will be broken into smaller particles. The sheared particles thus formed may have different surface properties and change the rate of flocculation as they accumulated. Gentle mixing (say 40 RPM) is sufficient to produce good floc. A decidedly better settled water (turbidity and floc size as determining criteria) is produced at this speed than at 60 RPM or higher speeds. Beyond 60 RPM, redispersion due to breakup of already formed flocs was noticed. Langlier⁴⁶ made a systematic study of flocculation process. He suggested the process of tapered flocculation, which was advocated by Camp as well. High velocity gradients give higher flocculation and can be conveniently used when the floc size is small. As the flocs grow in size, the velocity gradients should

be reduced progressively to allow further growth of the floc. The permissible initial velocity gradient and the steps in which its reduction should be achieved will depend upon type of impurities present, type and quantity of coagulation used and the size and nature of flocs desired⁴⁵.

2.7.3B Velocity Gradients During Flocculation:

The speed of flocculation and size of floc obtained are controlled by velocity gradients. Michales and Bolger³¹ studied the settling and plastic flow characteristics of flocculated Kaolin suspensions. They concluded that the tendency was, aggregate size to decrease as the velocity gradients increase, although change was small in the range of 21 - 42 sec^{-1} .

Camp and Stein³ specified the velocity to be a function of the drag coefficient of paddle, area of paddle, RPM of the shaft, velocity imparted to water, viscosity of water, and volume of the water. The optimum velocity for coagulation is usually found to be 0.5 to 1 fps.² Because floc will settle usually at velocities less than 0.3'/sec and will be broken up by velocities greater than 2.5'/sec.²⁴ As discussed earlier velocity gradients of the order of 10 to 100 sec^{-1} are generally used, at least when Al(III) or Fe(III) salts are used as coagulants. Optimum velocity gradient for flocculation is predominantly controlled by the chemical make up of the water⁵¹.

2.7.9 Flocculation Time:

Flocculation time is the time elapsed between the addition of coagulant to the water and at the end of the agitation of water at a velocity high enough to prevent settling of the flocculated matter.

Flocculation time is inversely proportional to the floc volume fraction, intensity of agitation, and collision efficiency factor¹.

Griffith and Williams¹⁸ reported that turbidity removals improve with increased flocculation detention time upto 30-35 min. When detention times were extended beyond 35 min, turbidity removal became progressively poorer. A flocculation time of 10 minutes with 40 to 60 RPM (or at optimum velocity gradient) was found most suitable by water chemists.

According to Camp and Stein³ (Gt), a dimensionless product is a critical parameter governing the flocculation process. It's significance and normal operating values has already been discussed in earlier sections.

2.7.10 Water Temperature:

Temperature has long been recognized as an important factor in treatment.

Camp, Root, and Bhoota³⁴ investigated the effect of temperature upon the rate of floc formation and concluded that changes in temperature (not near the freezing point) have no measurable effect on the time of floc formation, but both

settling and filtration efficiencies deteriorate with decrease in temperature near freezing. Generally colder the water, longer is the time required to produce good² floc with a given amount of coagulant. Rao's studies³⁴ indicate that for a given coagulant dose, a considerable shift in optimum pH was observed with change in temperature.

The alum dosage required at higher temperature are considerably lower than those required for the same degree of turbidity in a cooler water. Generally, speaking the lower the temperature of water the more retarded is the chemical reaction, and subsequent floc formation. A decrease in temperature increases the density and viscosity of water. It is increased viscosity more than increased density which is involved in above effect²⁷.

2.7.11 Summary:

From a critical review of the above, it appears that factors such as pH, velocity gradients and the presence of ions (cations and anions) in the water affect the coagulation process to a great extent. The effect of anions in water was found to extend the optimum pH range for coagulation to the acid region. pH of water affects the amount of precipitation and the time of floc formation through its effect on the charge of the particle. The rate of flocculation and the size of the

floc obtained are reported to be controlled by velocity gradients. Concentrated suspensions coagulate more easily than dilute suspensions. Alkalinity affect the process of coagulation to a great extent.

and as the model becomes more complex the need for design of experiments is magnified⁽⁴⁴⁾. Widely known experimental plans such as Factorial Designs are useful in making a preliminary survey of system variables⁽⁴⁾.

2.8.2 Factorial Design^(22,11):

Factorial designs can be applied to any number of factors and levels thereby enabling simultaneous determination of the effect of a large number of variables with possibly fewer runs. For a given accuracy, the factorial design greatly reduces the number of runs required, because of the advantage that all the results are utilized in calculating each effect.

There are five typical backgrounds, shown in Table 2.8.2, which characterize the evolution of a line of experimentation.

In every experiment there are two types of variables. These are the independent variables (process variables, factors) which are deliberately varied from run to run so as to take specified values denoted (X) and the resulting dependent variables (responses, product properties) denoted (Y).

The steps generally involved in research experimentation are:

Step 1: (Screening experiment)

Identify key variables.

Step 2: (Response-surface experiment)

Develop prediction equations.

TABLE 2.8.2: FIVE EXPERIMENTAL ENVIRONMENTS

Type of Experiment	Typ. no. of Independent Variables	Typical Information Sought	Typical Design
Screening	6 to 20 (continuous and/or discrete)	Identify which ones of independent variables are important; show approximate overall effect of each	Plackett-Burman
Limited Response Surface	3 to 8 (continuous and/or discrete)	Prediction over limited exptl. region, with estimates of linear effects and interactions only	2-level factorial (centre point can be included)
Response-Surface	2 to 6 (continuous)	Higher quality predictions over region where linear, interaction and curvature effects are needed	Box-Behnken
Theoretical Model	1 to 5	Estimate parameters in theoretical model to enable use outside range variables	Special-purpose computer-derived design
Sampling Experiment		Quantify contribution of various sources to the overall product variability under standard operating conditions	Nested or cross-classification

Step 3: Formulate 'theoretical' relationships for scale-up or extrapolation using previous technology and the results of Steps 1 and 2.

Step 4: (Non-linear design and estimation)
Test and refine theory, starting with Step 2 data and continuing with special purpose, computer derived designs, until confident of scale-up and extrapolation.

2.8.3 Advantages⁽²¹⁾:

Factorial designs have following main advantages:

- (1) Many variables may be studied at one time making it possible to gain insight into their simultaneous effect on responses of interest.
- (2) Interactions between variables can be determined, which is impossible, if the more common one-variable-at-a-time procedure is employed, where in turn, each variable is changed with all the remaining variables being held constant.
- (3) Useful direction of experimentation are often indicated which can be subsequently explored with profit.
- (4) Factorial and fractional designs have been found useful even at the very out set of experimentation when very little may be known about the system.

- (5) Designed experimental programs are efficient when the purpose is to screen variables those that are most important.
- (6) Because of the systematic and controlled procedures that are present in statistically designed experiments, interpretation of the results is often quite easy.

2.8.4 Factor Coding:

In order to simplify the writing procedure levels of the variables have been coded as '+', '-' and 0. In general, coding equations are written as:

$$X = \frac{(\text{Level of variable}) - (\text{Mid value of variable})}{\text{Unit of change}}$$

Low	Middle	High
-1	0	+1

Unit of change

Thus +1 denotes High level value
 -1 denotes Low level value
 0 denotes Middle level value

The size of the difference⁽²¹⁾ should be chosen consistent with the following two guides:

- (1) Make the change in a factor large enough to cause a significant change in an important response.
- (2) Make the change large enough to allow tolerable operating variability in controlling the factor, if it has no effect on an important response.

2.8.5 Construction of 2^k Factorial Designs⁽⁴⁾:

Box and Lucas presented a criterion, for designing experiments for the purpose of providing precise parameter estimates, in 1959.

In general, for k variables, one systematic way to write all possible combination of two-levels of the variables X_1, X_2, \dots, X_k for a 2^k factorial design is to proceed as follows:

- (i) For X_1 - Alternative positive and negative signs for all the 2^k tests
- (ii) For X_2 - Signs alternate in pair
- (iii) For X_3 - Signs alternate in groups of four
- (iv) For X_4 - First eight tests as -1, the next eight as +1 and so on
- (v) For X_k - First 2^{k-1} tests as -1^s and next 2^{k-1} tests as plus

2.8.6 Fractional Factorial Design⁽¹¹⁾:

For screening the experiment fractional factorial designs find much wider use, especially Two-Level design. The advantage of fractional factorial designs over factorial designs is that fewer runs are required. But what one gains in the number of runs, one loses in confounding.

- (A) Maximum number of variables that can be studied in using fractional factorial designs will be

<u>Number of Runs</u>	<u>No. of Variables</u>
4	3
8	7
16	15
32	31
64	63
128	127

(B) Construction of Two-Level 2^{k-p} Fractional Factorial Designs - Columns for first three parameters viz. X_1, X_2, X_3 remain same as factorial design. For new variable columns may be constructed as follows:

<u>Fractional Factorial Design</u>	<u>Column for new variable</u>
2^{4-1}	4 = 1.2.3
2^{5-2}	4 = 1.2.3, 5 = 1.2
2^{7-4}	4 = 1.2.3, 5 = 1.2, 6 = 1.3.7, 7 = 2.3

Similarly for higher orders columns shall be obtained. The total number of runs required in all above cases will be $2^3 = 8$.

2.8.7 The Mirror Image Design⁽²²⁾:

In fractional factorial designs new columns are obtained as discussed above. Hence main effect of parameters are confounded with two and three factor interactions effects. The main effects can be untangled from the second order interaction effects by switching the signs of all the elements of the design matrix for the previous eight tests; thereby obtaining

the mirror image design. This replication with reversed signs breaks all alias links between main effects and two factor interactions. The design matrix thus obtained specifies new conditions of eight further tests, thereby lessening the confounding effect.

The remarkable thing about running the first eight trials together with mirror image design is that it allows us not only to obtain the main effect of variable unconfounded with 2-factors interactions that were confounded with it after the first eight trials.

2.8.8 Randomization⁽⁴⁴⁾:

The main reason for randomization of trials is to take out insurance against influential conditions that might be changing.

2.8.9 Response Surface Concept⁽⁴⁴⁾:

In process studies it is often required to describe the response of one or more dependent variables to several independent variables. The relationship can be expressed by one or more mathematical equations or models. Models could be exact or approximate. The exact model is rarely known, therefore, empirical models must be used to approximate the response. Thus mathematical models are mathematical representation of the process.

The basic idea involves fitting a mathematical model to a collection of data using the sum of squares criterion. The

method of least squares is sometimes called regression analysis or surface fitting. By regression analysis the relationship between the changes made in input (independent variable) and the changes observed in the output (dependent variables) is obtained by trial and error or iterative procedure. Taylor series approximately are widely used and have been very valuable in analyzing research data.

For linear relationship two fits are commonly tested--ordinary fit and Log fit.

Equation for ordinary fit

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + \dots + B_kX_k$$

and, Equation for log fit will be

$$Y = \exp (B_0 + B_1X_1 + B_2X_2 + \dots + B_kX_k)$$

where B_0, B_1, \dots, B_k are constants.

Depending upon the error and confidence interval, involved, fit can be finally chosen.

Two-Level fractional factorial designs do not give any estimate of the curvature of the response in the experimental region. In order to estimate the curvature of each factor adequately, the number of runs in the design would be increased by 50 to 100%, however, a relatively economical estimate of the curvature of any or all factors can be obtained by running points at a middle value of all the factors. But, these centre points can be run only for continuous factor system. The severity of the curvature is estimated by the difference between

the average of the design points and the average of the centre points. If curvature is severe the estimates of the main effects and interactions can lead to predictions which may be greatly in error both inside and outside the experimental region.

Minimum significant curvature

$$C = t S \sqrt{\frac{1}{mk} + \frac{1}{C}}$$

where t is the value of students 't' at the desired probability level for the number of degrees of freedom in the estimate of the S .

m number of positive signs in the column m

k reflects for each trial and

C number of the centre points.

2.9 Basic Concepts of Statistical Methods in Engineering⁽⁴¹⁾

(1) Samples and Populations

Sample (one or more observations) is randomly selected from a population, statistical techniques enable estimates of the population parameters, and of the relationships among population parameters, to be made from the sample parameter from sample make statistical inferences about population.

(11) The Mean of a Sample

It is a measure of central tendency

$$\bar{Y} = \left(\frac{\sum_{i=1}^n Y_i}{n} \right)$$

(iii) The Variance of a Sample

A characteristic of great importance is the extent to which individual observations are spread about mean

$$S^2 = \frac{(Y_1 - \bar{Y})^2 + (Y_2 - \bar{Y})^2 + \dots + (Y_n - \bar{Y})^2}{(n - 1)} = \frac{\sum_{i=1}^n (Y_i - \bar{Y})^2}{(n - 1)}$$

or

$$S^2 = \frac{\sum_{i=1}^n Y_i^2 - \left(\sum_{i=1}^n Y_i\right)^2}{n(n - 1)}$$

The positive square-root of the variance is called (by definition) the standard deviation. It is some times desirable to describe the variability relative to the average. For this purpose the coefficient of variation, C.V. is defined to be (S/\bar{Y}) .

It is never possible to know exactly, from the observed quantities, still, sample mean and sample variance provide the most-efficient estimates of the corresponding population parameters (μ, σ, σ^2) .

2.9.1(A) Role of Theoretical Distributions in Statistical Methodology

Broadly speaking the methodology of statistical analysis encompasses the calculation of one or more appropriate statistics from a set of observations upon a physical system. These statistics are used in any of the following ways:

- (1) To provide estimates of the corresponding properties of the population from which data were drawn.
- (2) To construct upper and lower limit of each statistic within which the corresponding population characteristics are

to be found with a specified high probability.

(3) To test hypotheses about population characteristics, or relations among them.

2.9.1(B) Some Theoretical Distributions

Principal statistical distributions are: the Normal, the t -, the chi square and the variance ratio distribution.

(1) The Normal Distribution -- It is found in practice that random components in most data conform adequately well to a theoretical frequency distribution whose mathematical definition is

$$P_N(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-1/2 \left(\frac{x - \mu}{\sigma} \right)^2}, \quad -\infty < x < \infty$$

The normal distribution (often called "error function" or the Gaussian Distribution) is symmetrical bell shaped, about mean μ . Between -3σ to $+3\sigma$ 99.8% area is covered.

(11) The t -Distribution -- $t = \frac{\bar{X} - \mu}{S/\sqrt{n}}$ This quantity is called "students' t ", the frequency distribution ' t ' is symmetrical about 0. As n (number of observations) increases, the t distribution more closely approximates the normal distribution and converges to normal distribution when n is infinitely large.

(111) The Chi-Square Distribution --

$$\begin{aligned} &= \frac{S^2}{\sigma^2/f} = \frac{f}{2} \left(\frac{\sum_{i=1}^f (X_i - \mu)^2}{f} \right) \\ &= \sum_{i=1}^f \left(\frac{X_i - \mu}{\sigma} \right)^2 \end{aligned}$$

$$Z = \frac{(\bar{X} - \mu)}{S/\sqrt{n}} \quad \text{and} \quad t = \frac{(\bar{X} - \mu)}{S/\sqrt{n}}$$

χ^2 is the sum of squares of standardized normal derivatives.

Therefore, it is always positive in contrast to z and t .

(iv) The distribution of the Variance Ratio, F - The distribution of the variance ratio is the distribution of $F = S_1^2/S_2^2$ where $1 \leq f_1 < \infty$ and $1 \leq f_2 < \infty$.

$$t = \frac{\bar{X} - \mu}{S/\sqrt{n}} = \frac{\bar{X} - \mu}{S_2}$$

$$F = t^2 = \frac{(\bar{X} - \mu)^2}{S_2^2} = S_1^2/S_2^2, \quad (\bar{X} - \mu)^2 = S_1^2 = \text{Variance}$$

of single difference represented by the numerator has one degree of freedom associated with it and where S_2^2 is the variance of \bar{X} .

2.9.2 Construction of Intervals:

The construction of intervals and subsequent reporting of results in the form of intervals, is an exceedingly important part of practical statistical analysis.

(A) Confidence limits for population mean - The population parameters μ and σ are both estimated from sample values (\bar{X} and S) by the help of student's t distribution. 95% confidence limits ($\pm 2\frac{1}{2}\%$ in each tail) for μ shall be

$$\bar{X} - t_{0.975} (S/\sqrt{n})$$

$$\bar{X} + t_{0.025} (S/\sqrt{n})$$

Corresponding to the number of degrees of freedom associated with S , $u(n-1)$ and to the appropriate probabilities, here, 0.025 and 0.975, fractiles of the 't' distribution are used.

(b) Confidence limits for the population variance - In order to construct confidence limits for the σ^2 in terms of S^2 having f degrees of freedom, chi square distribution is used.

$$\frac{S^2}{\sigma^2} = \frac{S^2}{\sigma^2} \quad 95\% \text{ confidence interval will be}$$

$$\frac{S^2}{\chi^2_{0.975}/f} \leq \sigma^2 \leq \frac{S^2}{\chi^2_{0.025}/f}$$

2.9.3 Selection of Variables and Levels⁽⁴⁾:

The importance of judgement, in choosing the variables to study and the levels of variables and in selecting which variable to confound with which interactions, is obvious. These considerations and others like them play a vital role in experimentation, and there are no mathematical techniques which directly provide guidance for such decisions. Experience is the only answer. Design is undoubtedly of greater importance. The damage of poor design is irreparable; no matter how ingenious the analysis, little information can be salvaged from poorly planned experiments.

2.9.4 Design of Experiments in Sanitary Engineering:

Statistical experimental designs have been rarely used to sanitary engineering processes. Berthouex and Hunter^(7,8) have shown that well planned few observations to R.O.D. experiments, yield precise estimates of the parameters k & L_a . They have also concluded that the procedure can be of use to those processes which involve first-order reaction models and can be readily extended to more complicated models. But Hunter^(22,8) has also cautioned that widely known experimental plans such as factorial designs are not always applicable to the experimental situations that face sanitary engineers. Two level fractional factorial designs have also been used for filtration studies⁽²²⁾.

2.9.5 Two-Level Quarter Factorial Design for Five Parameters:

For two-level quarter factorial design for five parameters, number of runs required will be $2^{5-2} = 2^3 = 8$. If mirror design is also to be used the number of runs will be doubled i.e. 16.

The first three columns for X_1 , X_2 and X_3 will be as discussed earlier in Sections 2.8.5 and 2.8.6. New columns for X_4 and X_5 will be obtained by multiplying columns 1 and 2, 1, 2 and 3 respectively. Thus two generating relations, $I = 1.2.4$ and $I = 1.2.3.5$, define the above design. Defining relations, describe the confounding pattern for the design which tells what qualities are confounded with other quantities.

CHAPTER III

3.0 EXPERIMENTATION:

Clay imparts the most commonly encountered turbidity that must be removed from any water supply. As a rule most water works in India use alum as coagulant. Hence all laboratory experiments were conducted using a suspension of Kaolin, a negatively charged white powder, in water and with alum as the coagulant. Same stock of Kaolin and alum (Aluminium Sulfate L.R. Grade) was used through out the experimentation. Provision of Kaolinite for preparation of turbid suspensions eliminated the variations occurring, due to the changing nature of turbidity, in natural waters.

3.1

The primary purpose of this study, as stated earlier, was to measure turbidity removal as a function of several parameters of the environment in which the reactions occur. It was desirable therefore to standardize the procedures so that electro-chemical stability of the system would be constant from one run to the next. After preliminary investigations, the following procedure was adopted.

3.1.1 Colloidal Suspension:

The goal of developing a readily reproducible system, yielding a dense floc was attained by keeping finely ground

Kaolin soaked with water for several days. Everyday prolonged stirring was done to maintain the uniformity of the suspension. This well mixed suspension was allowed to stand almost for two hours. The supernatant was siphoned and subjected to continuous aeration for hours together and allowed to settle overnight. Compressed air from a central compressor was utilized for aeration purposes. Before beginning each test the stock Kaolin suspension was suitably diluted and aerated.

3.2

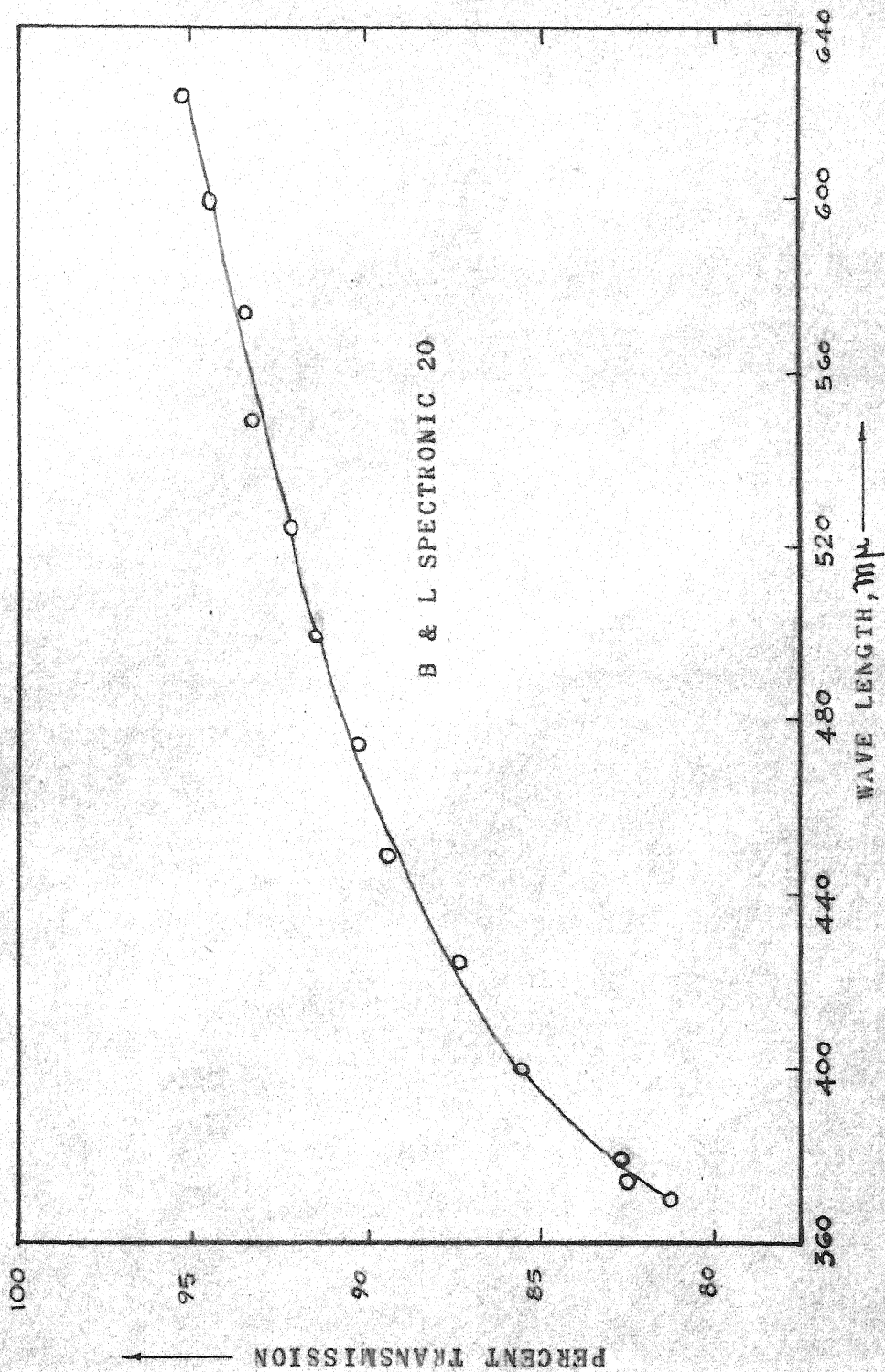
The chemistry of alum emphasizes the importance of coagulating at constant optimum pH and having adequate alkalinity present for hydrous polymers of aluminium to form. The buffering action in natural waters is primarily due to the presence of carbonic acid or CO_2 and its conjugate base - bicarbonate ion. This buffer system of carbonate-bicarbonate was manipulated to keep pH constant while altering the alkalinity of dilution water. Water used for preparation of suspension was of constant alkalinity, pH and composition. It was ensured that distilled water used for making various solutions was of uniform quality. Distilled water from laboratory unit was used throughout the experimental work. Every time before carrying out tests, alkalinity, pH, and turbidity were checked to keep same composition of the suspension.

3.3 MEASUREMENT OF TURBIDITY

The transmission characteristics of Kaolin suspension in distilled water were measured with spectrophotometer (Spectronic - 20 Bausch & Lomb). Minimum percent transmission at maximum instrument sensitivity was obtained at a wavelength of 370 millimicrons, as shown in Figure 3.3.1. A wavelength of 375 millimicrons was hence selected for use, as it would then be possible to compensate for any fall in instrument sensitivity.

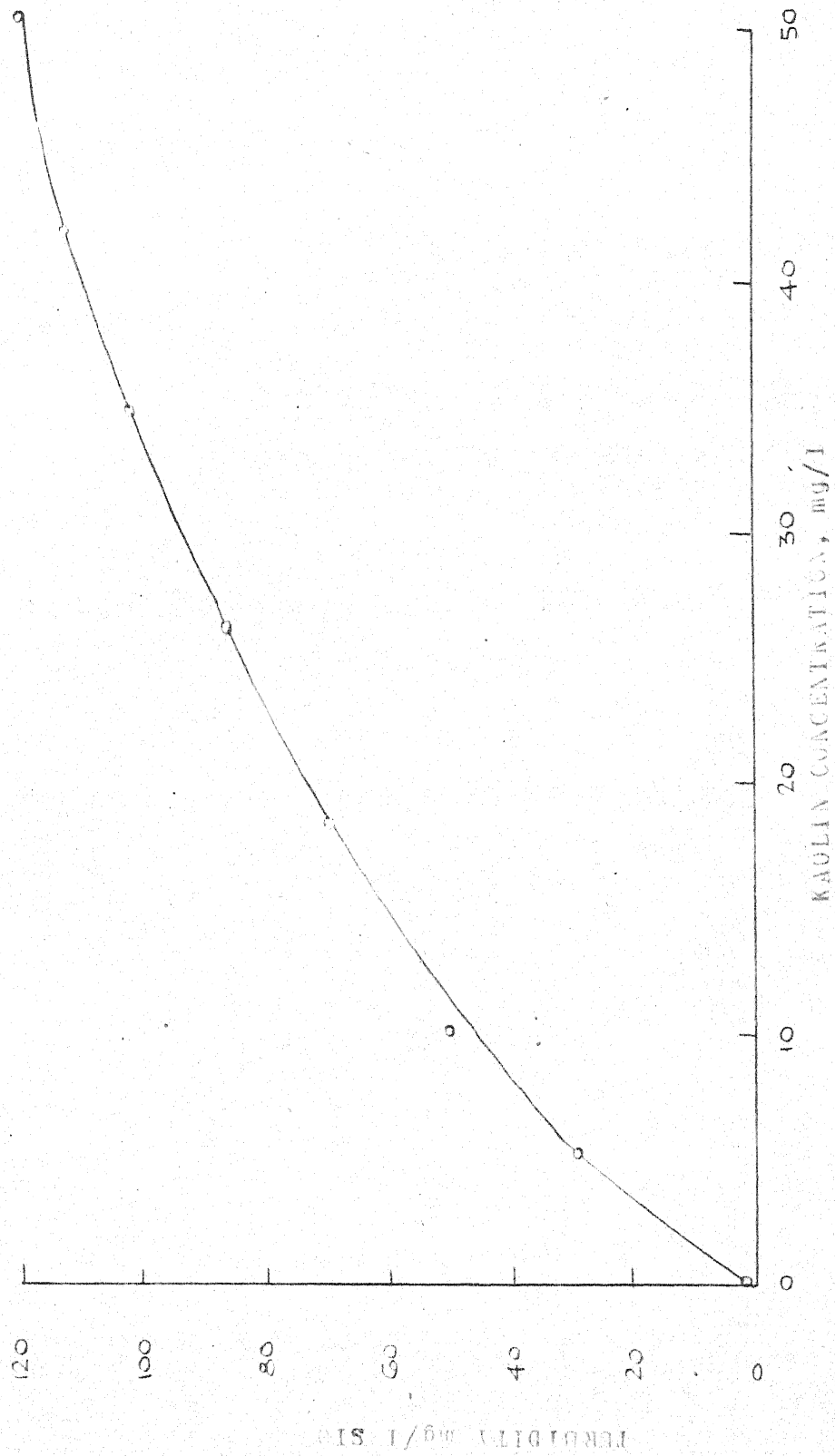
The relationship between Kaolin concentration and turbidity was determined by measuring turbidity with a Hellige Turbidimeter and filtering the same sample through a No. 42 filter paper. Filter paper containing Kaolinite was kept in an oven set at 105°C. Weight of the dried sample was taken after 48 hrs. In order to ascertain that moisture content is zero, sample was kept again in oven and weighed after lapse of 24 and 48 hours. The relationship between Kaolin concentration and turbidity is shown in Figure 3.3.2.

Figure 3.3.3., standard calibration curve for turbidity, presents the results of measurements made, at 375 millimicron, with suspensions of different concentrations of Kaolin in distilled water. Beer's law is not followed over the range of concentrations investigated.



TRANSMISSION CHARACTERISTICS OF A DILUTE SUSPENSION
OF KAOLIN IN DISTILLED WATER

Fig 3.3.1



RELATION BETWEEN KAOLIN CONCENTRATION AND TURBIDITY AS MEASURED WITH A TURBIDIMETER

Fig 3.3.2.

AT WAVE LENGTH 375mμ

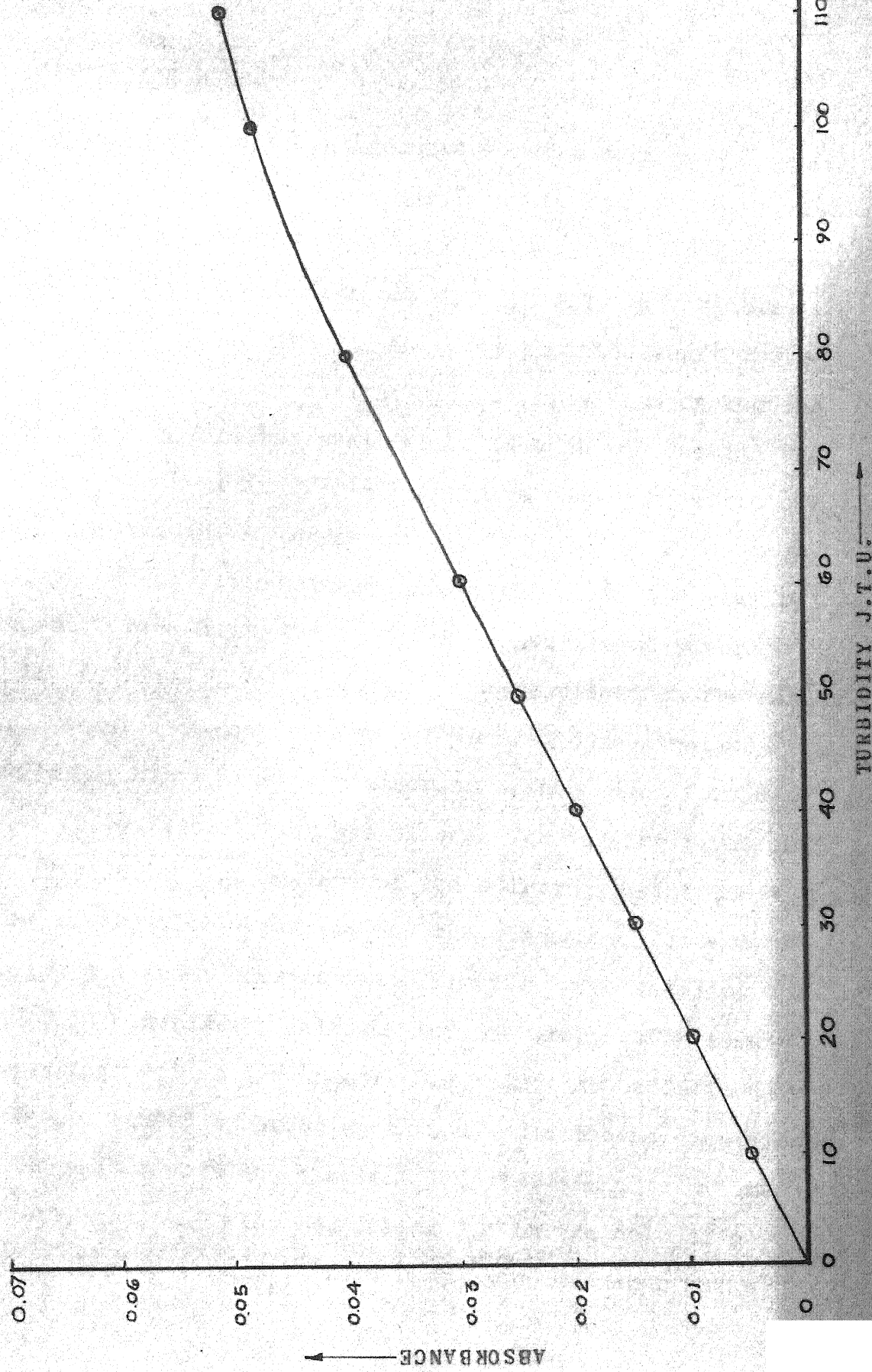


Fig 3.3.3

3.4 COAGULATION RUNS:

Laboratory experiments consisted of a series of conventional Jar tests using a multiple stirring apparatus with a controlled variable speed agitation system (Flocculator No. 75 - PHIPPS & Bird Inc. Richmond, Va, U.S.A.). A variable speed motor connected directly to the top of the shaft drove the paddle system at any desired speed. Provision of keeping six samples at a time was available. In each run one and the same sample was kept in five - containers while the sixth one was used for keeping a blank/control, in order to know the turbidity removal without coagulant by agitation and gravity settlement. Five hundred milliliter quantities of turbid water in one liter plastic containers were placed on the mixing stand. Measured dosage of alum, of desired concentration, was added quickly to each container and flash mixed for 30 seconds. Slow flocculation was allowed for varying times and speeds of paddles. At the end of the stirring period the containers were slowly removed and the flocs were allowed to settle for a standard period of 30 minutes. The settling period of 30 minutes was selected for use, because extremely long settling periods are undesirable, since the additional flocculation caused by Brownian motion would become significant. After the end of settling time i.e. 30 mts. aliquots of the supernatant, about 50 mls. was decanted with the help of a pipette. Samples were withdrawn from each container and a

fraction of them was mixed thoroughly to have one representative sample for measurement of residual characteristics, like alkalinity, pH, turbidity. Turbidity of each sample was also noted separately, finally averaging out the five readings. This step ensured against any irregularity occurring during addition of coagulant.

The sample for turbidity measurement was shaken violently for 15 secs before observation was made. Experience indicated that reproducible results could be obtained only if the floc was dispersed by violent shaking and hence this procedure was employed before all analyses. Turbidity in the coagulated sample was caused by alum floc, in addition to the turbidity caused by Kaolin. The determination of turbidity by spectrophotometer, pH by EILCO pH meter, and alkalinity by titration was done.

After completion of the settling and sampling schedule, the beaker contents were wasted. Containers were washed and rinsed thoroughly prior to the next run. The coagulation and flocculation was observed at several operating conditions and change in transmission characteristics was determined as a function of these variables.

3.5 DESIGN OF EXPERIMENTS FOR COAGULATION & FLOCCULATION

For the present study, it was decided, as already discussed in Chapter II, to study the effect of five important

factors on the percent turbidity removal over a limited experimental region. Two-Level Quarter Factorial with Mirror Design was chosen, since the design permits the assessment of several factors simultaneously with sixteen runs only.

The parameters chosen for the investigation purposes were: Initial turbidity, Alum Dosage, Alkalinity, Flocculation Time and speed of paddles. For each parameter two (high and low) levels were chosen, in accordance with the existing knowledge, and are shown in Table 3.5.1.

TABLE 3.5.1: HIGH AND LOW LEVELS OF VARIABLES

VARIABLES	UNIT	LOW LEVEL	HIGH LEVEL
1. Initial Turbidity	J.T.U.	20	200
2. Alum Dosage	mg/l or ppm	30	150
3. Alkalinity	mg/l as CaCO_3	100	450
4. Flocculation Time	minutes	10	30
5. Speed of Paddles	RPM	20	100

The design pattern used for this study is shown in Table 3.5.2.

CHAPTER IV

ANALYSIS OF DATA

4.1 Computation of Average Effects

Average effect of any of the factor is calculated by cross multiplying the appropriate column by the column of observations, summed algebraically and divided by the number of positive signs in the resultant column.

$$\text{Average Effect of } X_1 = \frac{\sum X_1 Y}{\text{No. of positive signs}} = \frac{\sum X_1 Y}{8}$$

Similarly other parameter effects as well as their interactions are found. Computation Tables 4.1.2 to 4.1.4 enable to calculate average effects of the parameters and their 2, 3 and 4 factors interactions. The column for $X_1 X_2$ (two factor interaction) is obtained by multiplying columns X_1 and X_2 together element by element. The columns for three and four factor interactions like $X_1 X_2 X_3$, $X_1 X_2 X_3 X_4$, etc. are also calculated in a similar way. The average effects are summarized in Table 4.1.5.

4.2 Estimation of Intrinsic Variability

To obtain a quantitative measure of the uncertainty in the calculated values for the effects and interactions the following quantities were calculated:

(A) The mean of observations

$$\bar{Y} = \frac{1353.1}{16} = 84.57$$

(B) The variance of observations

$$S^2 = 190.0$$

(C) Sample standard deviation

$$S = \sqrt{S^2} = \sqrt{190} = + 13.8$$

(D) Variance associated with any of the average effect

$$V = S^2/8 = 190/8 = 23.75$$

$$S_{av}^2 = 23.75$$

(E) Standard deviation for any average effect

$$S_{av} = (23.75)^{1/2} = + 4.9$$

(F) 95% confidence interval

95% confidence interval for any effect will be

$$= \text{Statistic} \pm t \text{ (estimated variance of the statistic)}^{1/2}$$

Since average effects are based on 15 degrees of freedom, for a 95% confidence interval the value of 't' is 1.753. Hence interval for main parameter will be as below:

$$\begin{aligned} \text{For } X_1 &= 4.163 \pm 1.753 \sqrt{23.75} \\ &= + 12.67 \text{ or } - 4.34 \end{aligned}$$

Similarly for other parameters the values be

$$X_2 : (29.77, 12.77)$$

$$X_3 : (-14.51, 2.49)$$

$$X_4 : (16.12, -0.88)$$

$$X_5 : (-12.99, 4.01)$$

Confidence Interval for Population Mean - Because of the symmetry of t-distribution

$$t_{0.025} = -t_{0.975} = -2.13$$

$$(t_{0.05/2} = t_{0.05/2} = t_{0.025} \text{ and } t_{0.975})$$

$$t_{0.025} = \bar{Y} - t_{0.975} (S/(n)^{1/2})$$

$$= 84.57 - 2.13 \times 3.45$$

$$= 77.22$$

$$\text{and } t_{0.975} = \bar{Y} - t_{0.025} (S/(n)^{1/2})$$

$$= 91.92$$

OR interval

$$P[\bar{Y} - t_{\alpha/2} S/\sqrt{n} < \bar{Y} + t_{(1-\alpha/2)} S/\sqrt{n}] = 1 - \alpha$$

$$P[77.22 < \bar{Y} < 91.92] = 0.95$$

This indicates that the probability is 95% that interval (77.22, 91.92) contains the population mean. The value of sample mean \bar{Y} is 84.57.

Confidence interval for population variance -

$$\text{From tables } \chi^2_{0.975} = 27.5$$

$$\text{and } \chi^2_{0.025} = 6.26$$

Degrees of freedom $f = 15$

$$\chi^2_{0.025} = \frac{s^2}{\chi^2_{0.975}/f} = \frac{190 \times 15}{27.5} = 103.5$$

$$\text{and } \chi^2_{0.975} = \frac{190 \times 15}{6.26} = 45.5$$

Probability is 95% that confidence interval (103.5, 45.5) contains population variance σ^2 .

Since replicates were not conducted there is no means of finding out the standard deviation. The method of Bennet and Franklin⁽⁶⁾ may be utilized where higher order interactions are assumed to be negligible. Assuming three and more factor interactions are negligible.

S.N.	Interaction	Effect	(effect) ² /16	D.F.
1	$X_1X_2X_3X_4X_5$	+60.90	231.25	1
2	$X_1X_2X_3X_5$	× 1353.1	× 11.44 × 10 ⁴	1-×
3	$X_1X_3X_4X_5$	-58.10	211.563	1
4	$X_2X_3X_4X_5$	-52.70	174.10	1
5	$X_1X_2X_3X_4$	+31.10	60.38	1
6	$X_1X_2X_4X_5$	-29.10	52.81	1
7	$X_1X_3X_5$	170.10	1806.25	1
8	$X_1X_2X_5$	-48.10	145.0	1
9	$X_1X_2X_4$	+41.10	105.63	1
10	$X_3X_4X_5$	+41.10	105.63	1
11	$X_1X_2X_3$	-35.90	80.63	1
12	$X_1X_3X_4$	-25.10	39.38	1
13	$X_2X_4X_5$	-25.10	39.38	1
14	$X_1X_4X_5$	+3.90	0.95	1
15	$X_2X_3X_4$	+3.90		
16	$X_2X_3X_5$	+33.10	69.344	1
			<hr/> 1172.90	<hr/> 16

$$\begin{aligned}\text{Standard deviation will be} &= 1172.90/16 \\ &= 7330.6\end{aligned}$$

By testing the main effects components of the sum of squares against calculated standard deviation, following variance dope are obtained

$$\begin{aligned}X_1 & 174.1/7820 = 0.022 \\ X_2 & 211.563/7820 = 0.027 \\ X_3 & 52.81/7820 = 0.0067 \\ X_4 & 114400/7820 = 146.5 \\ X_5 & 60.38/7820 = 0.0077\end{aligned}$$

The above analysis provides significant evidence that X_4 is the most significant of all the factors. Next in order are X_2 , X_1 , X_5 and X_3 .

4.2 Multiple Linear Regression Analysis

A multiple linear regression analysis of the data, for two fits, (Ordinary and Log) was carried out, by Computer. Results obtained, are discussed in Section 5.3.

TABLE 3.5.2: TWO LEVEL QUARTER FACTORIAL WITH MIRROR DESIGN
FOR FIVE VARIABLES

Trial Number	X ₁ Alum Dose	X ₂ Initial Turbidity	X ₃ Speed of Paddles	X ₄ Flocculation Time	X ₅ Alkalinity
1.	-1	-1	-1	+1	-1
2.	+1	-1	-1	-1	+1
3.	-1	+1	-1	-1	+1
4.	+1	+1	-1	+1	-1
5.	-1	-1	+1	+1	+1
6.	+1	-1	+1	-1	-1
7.	-1	+1	+1	-1	-1
8.	+1	+1	+1	+1	+1
9.	+1	+1	+1	-1	+1
10.	-1	+1	+1	+1	-1
11.	+1	-1	+1	+1	-1
12.	-1	-1	+1	-1	+1
13.	+1	+1	-1	-1	-1
14.	-1	+1	-1	+1	+1
15.	+1	-1	-1	+1	+1
16.	-1	-1	-1	-1	-1
17	0	0	0	0	0

In order to achieve good estimate of the significance of variables the trials were randomized and the following random order was chosen for the experimentation: 2, 7, 3, 14, 8, 6, 4, 11, 1, 13, 5, 10, 12, 16, 15, 9.

TABLE 4.1.1: EXPERIMENTAL DATA

(Response Y: Percent Turbidity Removal)

trial	Initial Turbidity JTU	RESIDUAL Turbidity Removal due to Gravity Settlement Only JTU	Residual Turbidity After Coag. & Floc. JTU	% Removal Taking into Account Gravity Settlement	% Removal Neglecting Gravity Settlement
1	20	19	1.5	92.2	92.5
2	20	17.6	4.6	74.0	77.0
3	200	195	23.0	88.3	88.5
4	200	170	03	98.3	98.5
5	20	17.0	04	76.5	80.0
6	20	17.0	04	76.5	80.0
7	200	170	04	97.8	98.0
8	200	176	11.5	93.5	94.25
9	200	190	06	97.0	97.0
10	200	164	07	95.7	96.5
11	20	19	06	68.5	70.0
12	20	17	09	47.0	55.0
13	200	160	5	97.0	97.5
14	200	200	12	94.0	94.0
15	20	17	2	88.3	90.0
16	20	19	6	68.5	70.0

TABLE 4.1.2: COMPUTATION TABLE

[illegible]

TABLE 4.1.3: COMPUTATION TABLE

(Three Variables Interactions)

[illegible]

TABLE 4.1.4: COMPUTATION TABLE

(Four Variables Interactions)

$X_1 X_2 X_3 X_4$	$X_1 X_2 X_3 X_5$	$X_1 X_2 X_4 X_5$	$X_1 X_3 X_4 X_5$	$X_2 X_3 X_4 X_5$	$X_1 X_2 X_3 X_4 X_5$	Trial
	+1				+1	1
	+1				-1	2
	+1				-1	3
	+1				+1	4
	+1				+1	5
Equi- valent to $X_4 X_5$	+1	Equi- valent to $X_3 X_4$	Equi- valent to $X_2 X_4$	Equi- valent to $X_1 X_4$	-1	6
	+1				-1	7
	+1				+1	8
	+1				-1	9
	+1				+1	10
	+1				+1	11
	+1				-1	12
	+1				-1	13
	+1				+1	14
	+1				+1	15
	+1				-1	16

TABLE 4.1.5: AVERAGE EFFECTS OF FACTORS FOR
TURBIDITY REMOVAL

No.	Factor	Av. Effect	No.	Factor	Av. Effect
1	X_1	4.163	16	$X_1X_2X_3$	-4.488
2	X_2	21.263	17	$X_1X_2X_4$	5.140
3	X_3	-6.01	18	$X_1X_2X_5$	-6.010
4	X_4	7.62	19	$X_2X_3X_4$	0.488
5	X_5	-4.49	20	$X_2X_3X_5$	4.130
6	X_1X_2	-1.64	21	$X_1X_3X_4$	-3.138
7	X_1X_3	0.49	22	$X_3X_4X_5$	5.140
8	X_2X_3	7.61	23	$X_1X_3X_5$	21.263
9	X_2X_4	-7.27	24	$X_1X_4X_5$	0.488
10	X_2X_5	0.488	25	$X_2X_4X_5$	-3.138
11	X_3X_4	-3.64	26	$X_1X_2X_3X_4$	3.89
12	X_3X_5	-4.163	27	$X_1X_2X_4X_5$	-3.64
13	X_1X_4	-6.59	28	$X_1X_3X_4X_5$	-7.27
14	X_1X_5	7.62	29	$X_2X_3X_4X_5$	-6.59
15	X_4X_5	3.90	30	$X_1X_2X_3X_4X_5$	7.62

CHAPTER V

5.0 DISCUSSION OF RESULTS:

5.1

Data for the percentage turbidity removal were obtained by a randomized two-level fractional factorial design with five control variables: initial turbidity, coagulant dosage, speed of paddles, flocculation time, and alkalinity. The results of the experiments were analyzed and effect of above important variables was studied with the help of Bar Charts.

5.1.1 Effect of Speed of Paddles and Flocculation Time on Turbidity Removal:

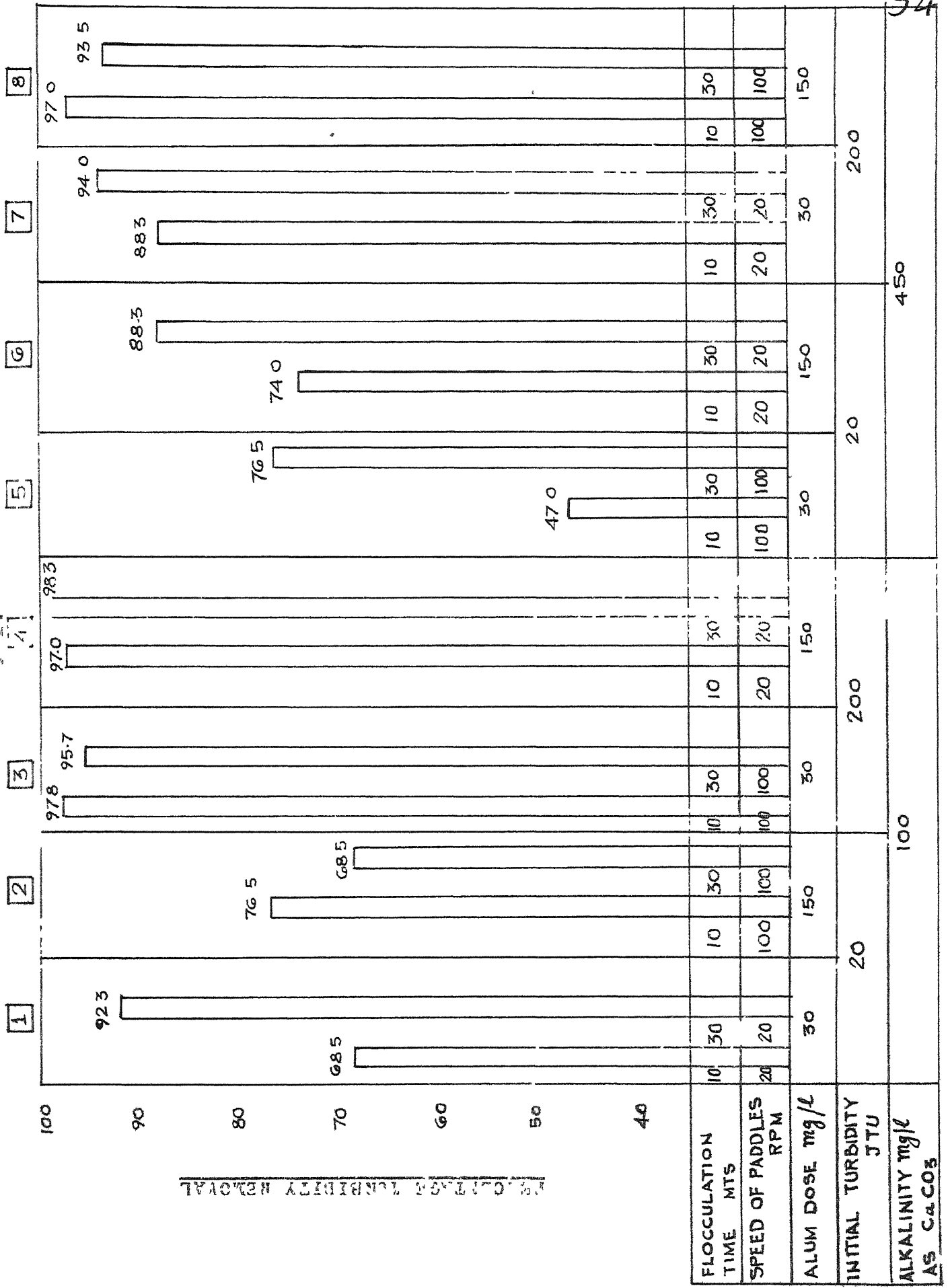
Bar chart I shows that, in general, as flocculation time increases, so does the percent turbidity removal, except in the case of run nos. 2, 3 and 8. The opposite trend observed in runs 2, 3 and 8 could be because of high speed of paddles in all these three trials, viz. 100 RPM. As discussed earlier, in the Literature Review Section 2.7.8.G (which depends entirely on paddle speed) has a marked influence on the rate of ortho-kinetic flocculation and the relation is described by the following equation:

$$\frac{-dN}{dt} = k_2 N \quad \text{where } k_2 \text{ is } (8\pi)v_f G$$

$$\text{or } N = N_0 e^{-k_2 t} = N_0 e^{-k_2 G t} \quad \text{where } k_2 = \frac{8}{\pi} v_f$$

BAR CHART - 1

EFFECT OF SPEED OF PADDLES & FLOCCULATION



Experience in water treatment practice has shown that value of G should be greater than $10 \text{ sec}^{-1}/\text{ft}$, in order to promote flocculation, but less than $75 \text{ sec}^{-1}/\text{ft}$, if disintegration of floc by shear is to be avoided. Optimum value appears to lie between 30 and $65 \text{ sec}^{-1}/\text{ft}$ with a minimum detention time of 10 minutes. Longer detention times, 30 mins or more are indicated for lower values of G and there is reason to believe that for satisfactory performance the dimensionless product GT may range within 10^4 to 10^5 .

At 100 RPM, differential velocity V_d is 2.0 fps and G comes to $750 \text{ sec}^{-1}/\text{ft}$, the product GT for this condition varies from 45×10^4 to 135×10^4 depending on the flocculation time.

Though through literature survey it has not been possible to determine accurately the maximum stirring velocities of laboratory stirrers, which will produce the quickest settling flocs, even then there are indications, based on working of water treatment plants, that figure is 1.0 to 1.3 fps for the tips of the stirrer blades. At any rate, in experiments using a speed as high as 2 fps, it was found that flocculated particles stopped growing at a much smaller size than that essential for rapid settling. Too vigorous agitation tended to lead to the disintegration rather than agglomeration of the growing floc particles. Thus the observation; in case of Trials 2, 3 and 8, of reduction in the percent turbidity removal

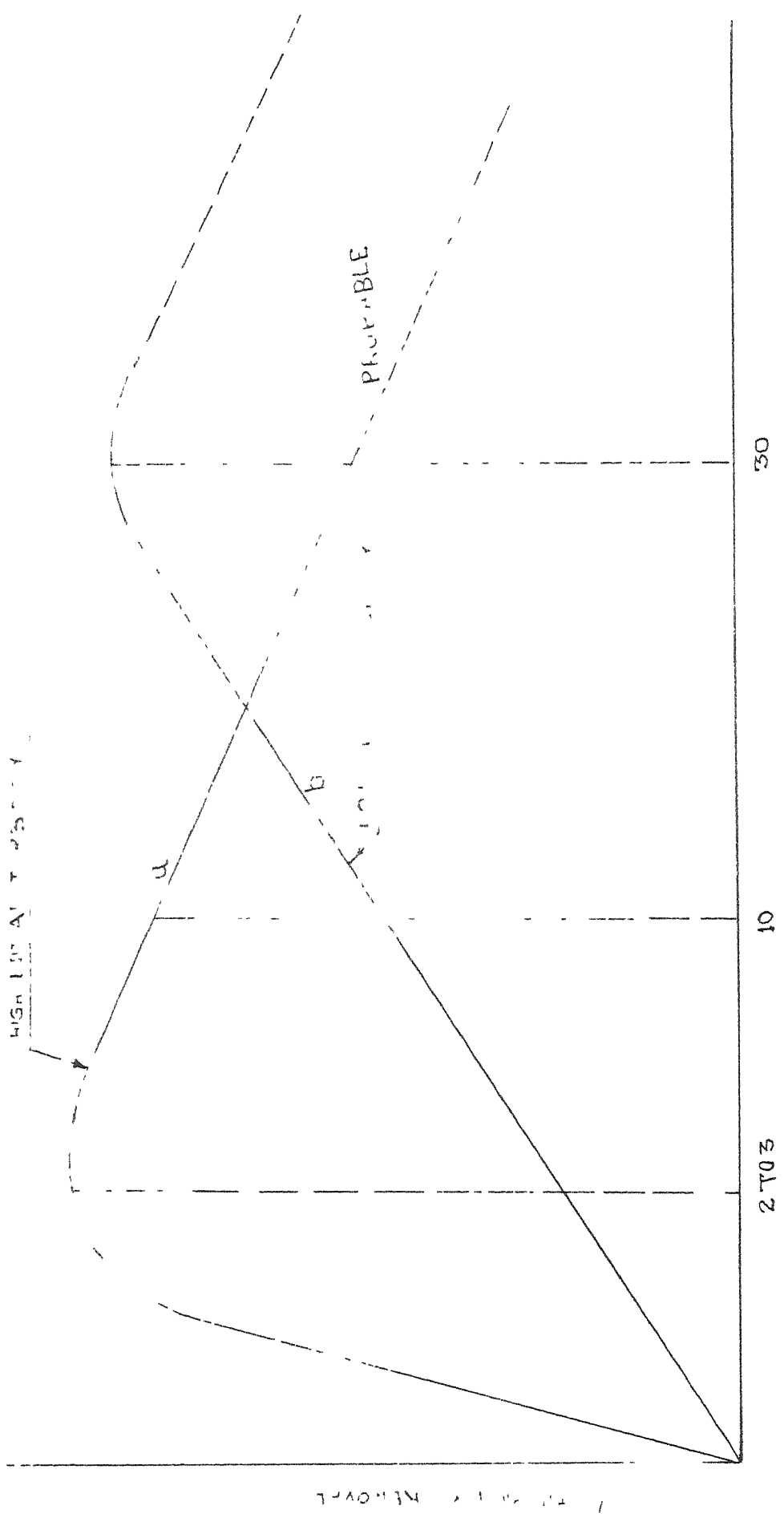
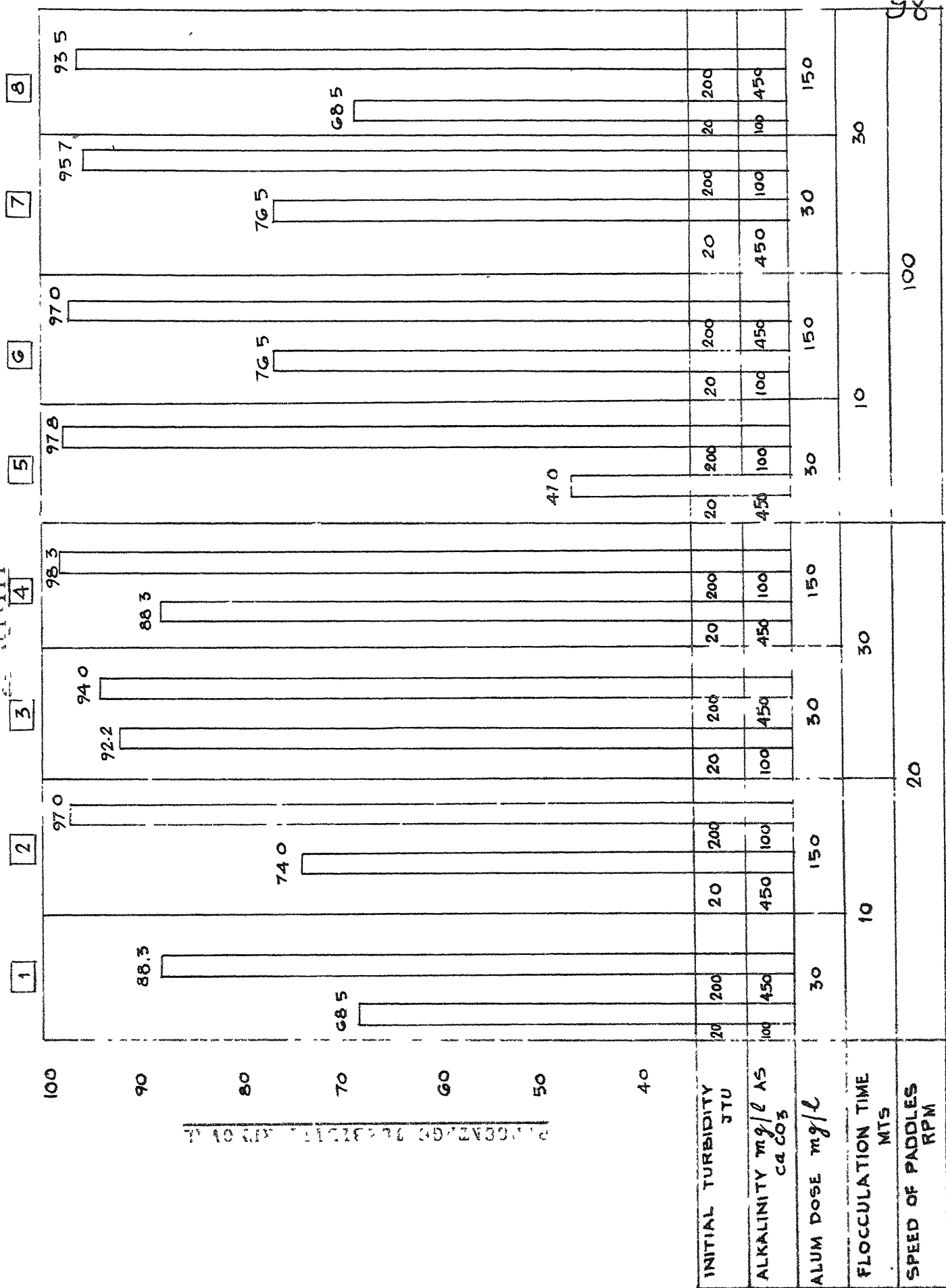


Fig. 5.11

BAR CHART - 2

EFFECT OF INITIAL TURBIDITY AND FLOCCULATION TIME

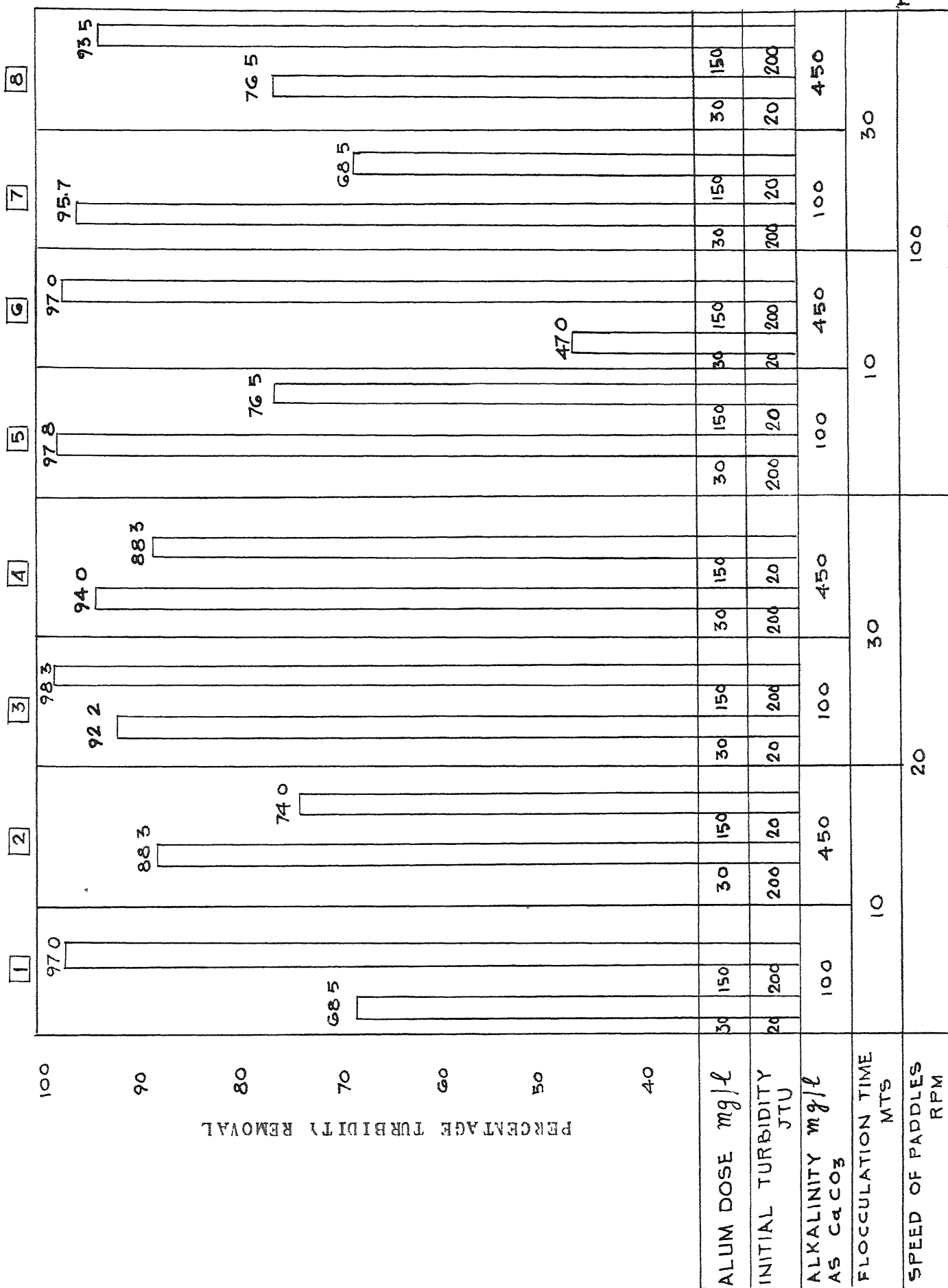


increases, higher percent removal of turbidity is obtained, in the range of experiments done for this study i.e. 20 JTU to 200 JTU. However, the extent of improvement in percent removal by an increase in initial turbidity from 20 JTU to 200 JTU, varies very much from case to case. In case (5), a marked improvement in percent removal by almost 51% is observed, by increasing the initial turbidity. Here the percent removal with low initial turbidity was extremely poor-4%, probably due to high alkalinity and a relatively low alum dose.

1 g.p.g. (17.1 mg/l) of alum theoretically requires only about 8 mg/l of alkalinity, whereas, experience indicates that better removals will be obtained if 10 or 12 mg/l of alkalinity is available. Hence for 30 and 150 mg/l of alum doses, desired alkalinity shall be about 21 and 106 mg/l as CaCO_3 respectively.

The rapidity of hydrolysis process depends upon the alkalinity present. Since alkalinity adds ions to the solution, it may change the charge on the colloids present. It is also the experience of chemists that alkalinity increases the amount of negative charge on the negative colloids. Moreover, due to high alkalinity present, pH will generally remain in neutral region, where the hydroxometal polymers are not highly charged, hence charge neutralization becomes difficult. At neutral pH range only effective phenomenon is adsorption. Hence association of high alkalinity with low initial turbidity results in poor removals, such as the case 5,

EFFECT OF ALUM DOSE & INITIAL TURBIDITY



where alkalinity is almost 22 times than what is desired. Overall percent turbidity removal picture is better in case 3, where alkalinity and turbidity are more consistent with each other. In conformity with above discussion, we find in general, that association of high alkalinity with low initial turbidity (450, 20) gives lower removal than that of low alkalinity and low initial turbidity (100, 20) association.

Comparison of 2 and 4 reveals that (450, 20) association gives higher removal. The higher removal in these cases could be attributed to increase in flocculation time.

The association of high alkalinity with high initial turbidity normally results in higher percent removals, which could be expected as per existing knowledge about flocculation process, e.g. 8, 6 and 3.

5.1.3 Effect of Alum Dose and Initial Turbidity on Turbidity Removal

By referring to Bar Chart 3, it is found that an increase in alum dose increases the percent turbidity removal. However, in several trials a negative response was observed, that is, an increase in alum dose resulted in lower removals, such is the condition with run nos. 2, 4, 5 and 7. In these cases following two associations 5 and 7 are marked.

Case 2: Excessive alum dosage restabilizes the colloid as a positively charged sol. as given in Section 2.7.1.

Case 4: The reverse trend is really not very well explicable. It seems that for this high initial turbidity; high alkalinity; high alum dose and high flocculation time, the floc formation is good and rapid indicating that either reeptization or shearing occurs to a small extent.

Above view point is greatly strengthened in association of low alum dose with high initial turbidity. Higher % removals are observed indicating that with high initial turbidity alum dose does influence removal, but to a very limited extent. The high initial turbidity is responsible for larger number of flocs, hence higher removal.

The minimum removal 4% in case 6, is due to low alum dose, low initial turbidity and high alkalinity combination. As explained earlier cumulative effect of all these parameters gives rise to such a poor removal. Percent removal is improved, as per expectation by associating high initial turbidity with high alum dose and high alkalinity.

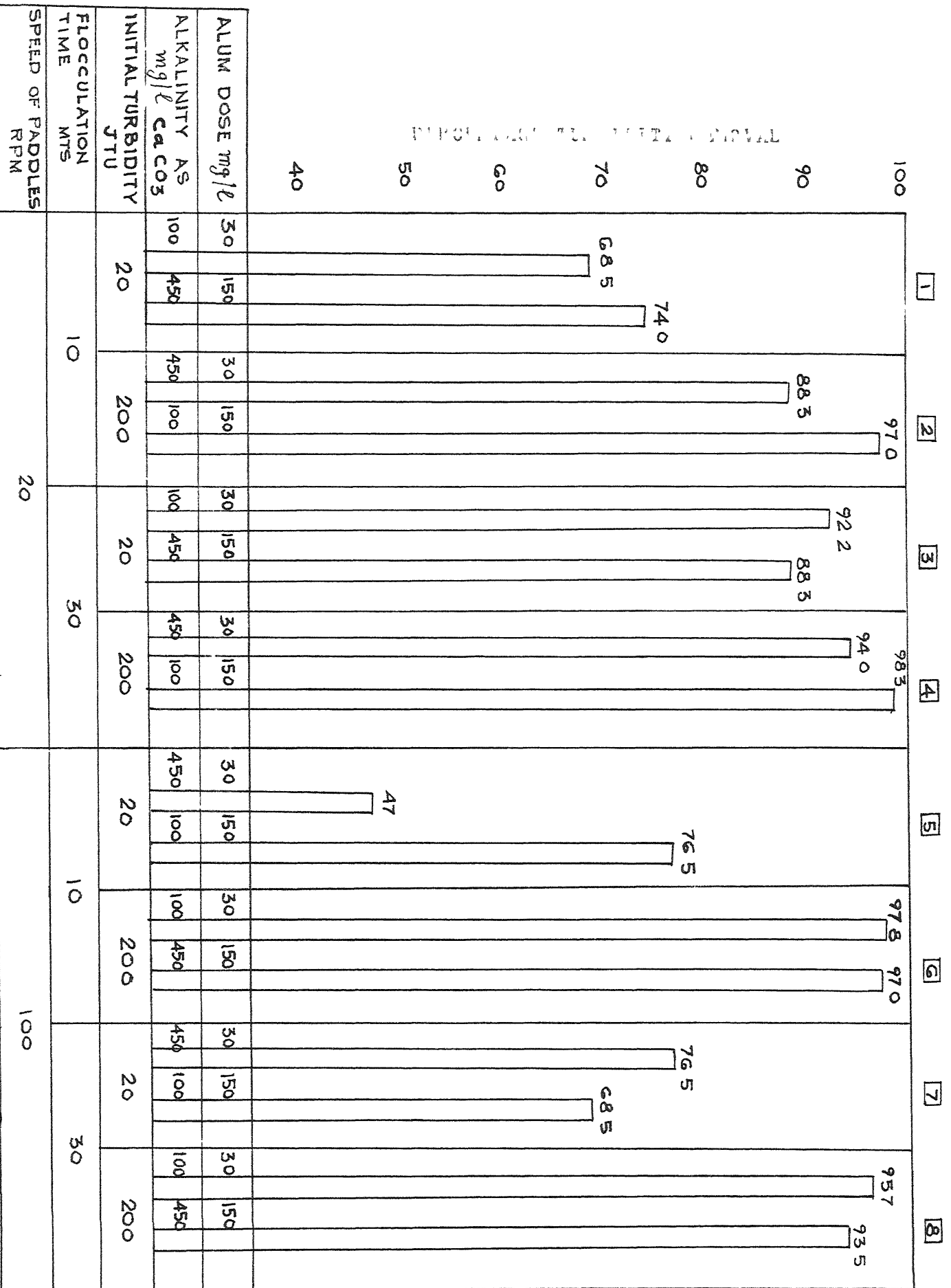
5.1.4 Effect of Alum Dose and Alkalinity on Turbidity Removal

As discussed in Section 5.1.3, it is observed again that with increase in alum dose, percent turbidity removal also increases except in four cases: 3, 6, 7 and 8.

As per theory alum dose and alkalinity bear a direct relationship i.e. an increase in alum dose necessitates the presence of higher alkalinity. In trials 3 and 7, because of

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a very low initial turbidity, the higher alum dose seems to result in reeptization. In 8, the higher alum dose may give much faster floc formation and disintegration at this high speed of paddles (100 RPM). In number 6, difference is insignificant.

5.2 Discussion of Statistical Factor Effects

From the computations (refer to Table 4.1.5), it is observed that the largest effect in absolute value is the one associated with X_2 (initial turbidity), which in turn is associated with three factor interaction $X_1X_3X_5$. This effect is 21.263, positive, which indicates that on the average, when initial turbidity was increased the percentage turbidity also increased. It may, however, be stated that the above effect may either due to X_2 or due to combination of $X_1X_3X_5$. It can not be said with assurance that this effect is entirely due to X_2 alone.

The other possible interpretation, of above result, is that this effect is only due to combination of $X_1X_3X_5$ only and that variable X_2 has no appreciable effect on turbidity removal. The third explanation could be that both of these (X_2 and $X_1X_3X_5$) are equally important and hence carry same weightage in turbidity removal.

In other words, if we neglect three factor interaction, one simple conclusion of the results obtained, apart from experimental error, from sixteen runs is that variable X_2 exhibits appreciable influence on the turbidity removal and is the key variable. This conclusion seems quite logical

"Higher the initial turbidity higher is the removal."

The next larger value is 7.62, which is associated with average effect of X_4 (flocculation time) and is also associated

with the string of two factor interactions X_1X_5 and X_2X_3 (assuming five factor interaction is negligible). The next largest quantity is 6.01 which is associated with variable X_3 (speed of paddles). One tentative conclusion could be made is that variable X_2 and X_3 are the two important variables which affect turbidity removal, and not only their individual effects are important, but also their interaction X_2X_3 is also important.

The next higher quantities are 4.49 and 4.16 associated with X_5 (alkalinity) and X_1 (alum dose) respectively. Thus their two factor interaction X_1X_5 is less important as compared to X_2X_3 . According to this interpretation, then in the string of two factor interaction X_1X_5 and X_2X_3 , the more important will be X_2X_3 . The other possible interpretation of data at this stage could be. The fact that the main effects of the variable X_1 and X_5 appear slightly less than that of X_3 , does not preclude the possibility that their two factor interactions are less important. Thus effect 7.62 could be (i) due to X_4 alone, (ii) combined effect of X_4 , X_1X_5 and X_2X_3 , and (iii) X_1X_5 and X_2X_3 or individually, they are important.

Similarly other observations from table can be effect of $X_1 \Rightarrow$ effect of $X_2X_3X_5$ combination, effect of $X_3 \Rightarrow$ effect of $X_1X_2X_5$ combination effect of $X_5 \Rightarrow X_1X_2X_3$.

Thus it is seen that effect 4.16 may be due to X_1 alone or due to combinations of $X_2X_3X_5$ or both are affecting symbiotically. If three factor interactions are neglected.

This is an assumption that is often made in practice, and it seems reasonable then it can be stated that effect is due to X_1 alone.

Similar explanation could be forwarded for X_3 and X_5 as well.

Thus at this stage there is no way to be absolutely sure of which variables and which multi factor interactions are of importance. In fact, it estimates both of these quantities together.

But while interpreting the magnitudes of the average effects and interactions one should always remember that these values are relative to the ranges of variables that were used and sizes of the effects are relative to the experimental ranges used. For example, if just because the effect of one variable is the largest in absolute value does not necessarily mean that **is** the most important. It may be that range employed for that variable is large. Some may be negligible at least over the ranges that were studied.

The 95% confidence intervals for μ and σ are small thereby indicating that these are nearer to sample values.

The 95% confidence intervals for parameters are wide. This implies that true difference may be much. The calculation indicates that there is no conclusive evidence either way.

Incidentally, it is rare that a problem is completely solved in all details. The present problem is realistic and

typical in this respect. But the important point illustrated in the results is that valuable information on the relative importance of the many variables had been obtained.

5.3 REGRESSION ANALYSIS

The multiple linear regression analysis was carried out for the experimental data on digital computer. Two fits- the ordinary fit and the log fit- were tried. The results showed that ordinary fit is better than log fit.

For ordinary fit the relationships are:

$$\begin{aligned} Y = & 66.99 + 0.3448 X_1 + 0.1354 X_2 - 0.1915 X_3 \\ & + 0.8244 X_4 - 0.0128 X_5 + 0.00106 X_2 X_3 \\ & + 0.004 X_2 X_4 \end{aligned} \quad (A)$$

(The coefficient of regression R^2 comes to 0.8620 which is quite close to the ideal value of 1.0 showing a close compliance or reliability of the fit)

Or if only individual parameters were considered and interactions of two or more parameters were ignored

$$\begin{aligned} Y = & 68.895 + 0.0345 X_1 + 0.1181 X_2 - 0.0752 X_3 \\ & + 0.38 X_4 - 0.0123 X_5 \quad (R^2 = 0.7245). \end{aligned}$$

$$\begin{aligned} Y = & 45.882 + 2.571 \ln X_1 + 28.589 \ln X_2 + 7.572 \ln X_3 \\ & + 14.975 \ln X_4 - 2.984 \ln X_5 - 11.31 \ln X_2 X_3 \\ & - 8.05 \ln X_2 X_4 \quad (R^2 = 0.7245). \end{aligned} \quad (B)$$

By comparing the two coefficients R^2 relationship (A) should be accepted.

T-values for relationship (A) are

For $X_1 = 1.11$, $X_2 = 2.4282$, $X_3 = -2.6023$, $X_4 = 2.8014$
 $X_5 = -1.2040$, $X_2 X_3 = 2.0424$, and $X_2 X_4 = -1.9485$.

From 'T' values it may be concluded the significant factors in order of importance are: X_4 (Flocculation Time), X_3 (Speed of Paddles), X_2 (Initial Turbidity), X_1 (Alum Dosage), X_2X_3 (Initial Turbidity, Speed of Paddles), X_2X_4 (Initial Turbidity, Flocculation Time), and X_5 (Alkalinity).

But effect of X_3 , X_5 on the response (viz. percent turbidity removal) is negative, which is in conformity with the existing knowledge. Increase of either X_3 or X_5 beyond optimum values, results in poor removals.

The positive effect of X_4 , X_2 and X_1 is in close conformity with the experience of sanitary engineers.

Well-established relations, relating various important parameters of coagulation and flocculation systems, as found in literature include

(1) Removal $\propto e^{\text{Product of Speed of Paddles and Flocculation Time}}$

(11) Dose of Alum $\propto (\text{Initial turbidity})^{\frac{1}{2}}$

Some relationships were also developed by Kawamura and Hanna⁵² based on their studies on colored and turbid suspensions. Parameters studied were turbidity, color, pH, alkalinity, colloid charge and electrophoretic mobility. The following are his equations relating optimum alum dosage, D, Total Alkalinity of raw water, A and colloid charge 'C' (expressed in meq/l $\times 10^4$).

(A) $D = \frac{1}{2} A + 1.37 C$ where color $>$ turbidity

(B) $D = \frac{1}{2} A + 0.411 C$ for turbid waters with low color

and

(C) $D = A + 0.453 C$ for colored waters with practically no turbidity.

Based on above relationships it may be assumed that the

Dose of alum (X_1) bears a direct proportionality to initial turbidity (X_2), and total alkalinity of raw water (X_5). Hence the possible linearship could be

$$Y = K_0 + K_1 X_1 + K_2 X_2 + K_5 X_5$$

Comparing it with (A) it is clear that both are in close agreement as far as nature of relationship is concerned. Though it is also known that turbidity removal is having exponential relationship with ($X_3 X_4$) i.e. GT, but this is true only for this product. It is quite likely that when combined effect of all the five parameters is considered, the relation (A) becomes much more significant, especially in the conditions of the present study.

CHAPTER 6

CONCLUSIONS

This investigation mainly indicates that if statistical methods of Design of Experiment are utilized to scientifically plan the experiments, high quality estimates, of the influence of various parameters for a process such as coagulation and flocculation, are obtained with a minimal experimental effort. For screening purposes of the parameters for any new process including sanitary engineering processes, Two-Levels Factorial Design can successfully be used.

Other important points illustrated by this study are:

- (1) That valuable information on the relative levels of significance of important variables in a process can be obtained
- (11) Parameter interaction effects can also be detected and evaluated quantitatively, which is not possible if one-variable-at-a-time approach is followed as is usually done by sanitary engineers
- (111) All main effects will be valid for the entire region of the experiment. Thus results once obtained are more generally applicable.

CHAPTER 7

SCOPE FOR FURTHER STUDY

In this study the Two-Level Quarter Factorial design was used as a first step for making a preliminary survey of coagulation and flocculation system variables. The data obtained does not yield the exact quantitative relationship showing the free effect of variables, it merely determines the effect. Hence for more exact relationship among all important variables recommendations, for further study in this area, are listed below:

(A) Replicates must be done to check the reproducibility of the results.

(B) The study should be extended to envelope more number of variables and wider range of values, viz. colloid charge (Zeta Potential), pH natural turbidity, coagulant aids and time and speed of rapid mixing.

(C) Regression analyses should be carried out on additional experimental runs at several levels so that more exact relationships could be determined.

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